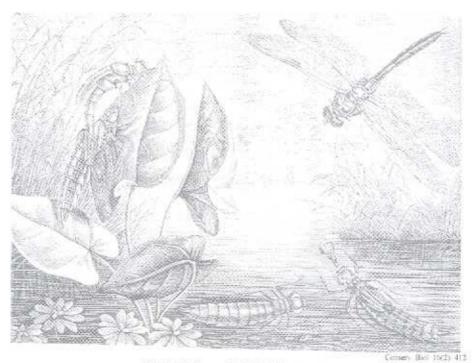


# U.S. Fish and Wildlife Service Region 2 Contaminants Program



## CONTAMINANTS IN FISH AND BIRDS OF WATSON LAKE, ARIZONA 2000 - 2001

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#### **ABSTRACT**

A wood treatment facility located on Yavapai-Prescott Indian Tribe land near Prescott, Arizona released pentachlorophenol (PCP), arsenic, and chromium into the environment from 1961-1985. We sampled sediment, water, fish, crayfish, eggs, tadpoles, and frogs for trace elements, organochlorine insecticides, polyaromatic hydrocarbons, total polychlorinated biphenyls, dioxins, and furans. Levels of arsenic, chromium, copper, and nickel remained elevated in sediment samples just below Slaughterhouse Gulch, which empties into Granite Creek just below the wood treatment facility. Crayfish are bioaccumulating mercury and selenium in Granite Creek. Granite Creek fish were highly contaminated with arsenic. Although copper was elevated in fish, concentrations were not high enough to exceed toxicity thresholds. Chromium contamination in fish was also evident, although the significance of the chromium concentrations remains unclear. High mercury concentrations were found in fish in Granite Creek and Watson Lake that could affect sensitive fish-eating predatory birds. Fish pentachlorophenol residues were lower than suggested regulatory guidelines. Only three dioxins and furans were detected in fish samples. Currently, soils from the on-site pond and work area are being bioremediated and, as soon as PCP levels reach Arizona non-residential soil remediation levels, the site will be re-contoured and re-opened to the tribe.

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#### INTRODUCTION

Southwest Forest Industries operated a wood treatment facility on 10.3 hectares (25.5 acres) of leased Yavapai-Prescott Apache Tribe land from 1961 to 1985 (Water Resources Associates, Inc. 1993). Operations involved the pressure treatment of logs and timbers with PCP in No. 2 diesel oil, PCP in methylene chloride, or PCP with a solution of copperchromated arsenate. Concentrations of PCP ranging up to 1,400 ppm were found in the onsite pond sediment (Western Technologies 1986). PCP was detected in ground water above 5 μg/l (Water Resources Associates, Inc. 1993). An U.S. Environmental Protection Agency (EPA) Administrative Order on Consent for this site established PCP cleanup standards at 11 ppm for soil and 1 ppb for water. In February 1985, Southwest Forest Industries completed Interim Status Closure Procedures and was granted a Resource Conservation and Recovery (RCRA) "clean closure" by EPA. The RCRA closure did not address the pond and other historic areas of contamination at the site. Subsequent to closure of the facility, petroleum hydrocarbon-containing soils were dumped on the site. In August 1991, the Yavapai-Prescott Indian Tribe hired a consultant to sample the pond water and sediment. Laboratory analysis of water and sediment revealed the presence of elevated levels of PCP, arsenic, chromium, polyaromatic hydrocarbons, total petroleum hydrocarbons, dioxins, and dibenzofurans (Western Technologies 1986, Water Resources Associates, Inc. 1993). The former wood treatment facility is currently an EPA designated Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) site. The projected completion date for full remediation was December 1999.

Granite Creek is the only major area watercourse that flows through the CERCLIS site and is located about 500 meters (1640 feet) downgradient from the former wood treatment facility. Granite Creek exits Tribal lands, and then flows through an area known as Watson Woods to Watson Lake and eventually to the confluence of the Verde River. Watson Woods is owned by the City of Prescott and has been leased to the Prescott Creek Preservation Association for 30 years. The riparian area contains mature cottonwood trees with a lush understory of willows and other mixed hardwoods, shrubs, and grasses. Several small marsh areas contain bulrush and cattail. Great blue herons nest in cottonwood trees at the confluence of Granite Creek and Watson Lake and several other waterbird and riparian species including wintering waterfowl, double-crested cormorant, coot, and killdeer are common in the area. A colony of cliff swallows nests under a bridge located less than 300 meters (984 feet) from the former wood treatment facility on Reservation land.

While water and soil on-site was extensively sampled by contractors, there were no studies of contaminants in fish and wildlife. In early June 1995, Environmental Contaminants staff from the Arizona Ecological Services Field Office were requested by Partners for Wildlife project personnel to assess contaminant concentrations in fish and wildlife from the then proposed Watson Woods Partners for Wildlife project area located in the Watson Woods portion of Granite Creek. Samples of crayfish and fish (fathead minnows) were collected from two locations on the creek. Crayfish and fish from both sites contained above

background levels of PCP, chromium and copper (Reference Tables 1 and 2). Pentachlorophenol, chromium, and copper are EPA designated Priority Pollutants.

#### STUDY AREAS

This study focused on fish and wildlife exposures to historical discharges from the abandoned Southwest Forest Industries wood treatment facility on Granite Creek; there are other point/non-point source dischargers on Granite Creek, as well. The Veterans Administration (VA) facility is farthest southwest on Granite Creek. Moving northeast along Granite Creek, the Superfund site is 2.84 kilometers (1.76 miles) from the VA. The wastewater treatment plant is 1.37 kilometers (0.85 miles) downstream from the Superfund site. The wastewater treatment plant discharges into Watson Lake and the lake empties into the Verde River 29.28 kilometers (18.19 miles) downstream. Our study sites included two Granite Creek locations, one upstream and one downstream, Watson Lake, and Lynx Lake. The upstream location, Site 1, was adjacent to an industrial park with access to the Creek, and was below all of the potential polluters. The downstream location, Site 2, was near the Watson's Woods parking lot. Site 3 was Watson Lake; this was the furthest downstream. Figure 1 presents the sampling locations and proximity to historical dischargers. Lynx Lake is not connected to this system. It is 7.68 kilometers (4.77 miles) away from Watson Lake and, therefore, served as a comparison site for this study. Sampling efforts focused on availability of biota and collections were made in 2000-2001.

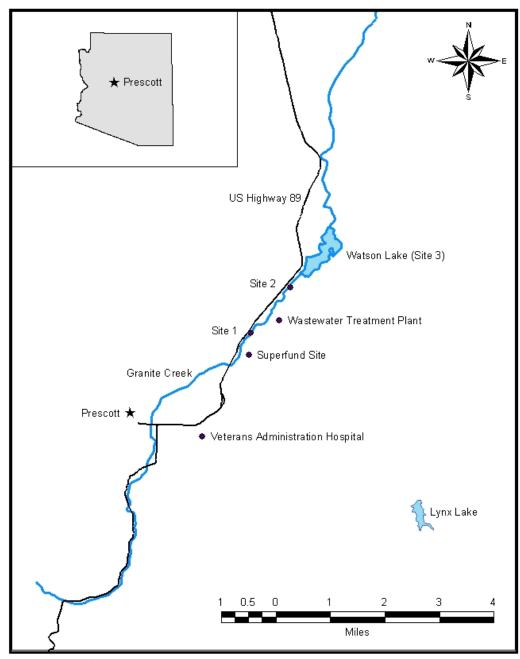


Figure 1. Samples sites along Granite Creek and at Watson Lake, near Prescott, Arizona, in 2000 and 2001.

#### METHODS

Sample collection and preparation-

Field collections were completed at all sampling locations from April 26 to July 19, 2000 and May 20 to August 21, 2001. We collected samples in the summer when water levels were higher and species were more abundant. We collected sediment samples from Sites 1 and 2 and a black phoebe (Sayornis nigricans) egg from Site 1 in Granite Creek. Northern crayfish (Oronectes virilis; Inman et al. 1998), fish [golden shiners (Notemigous crysoleucas), green sunfish (Lepomis cyanellus), bluegill (Lepomis macrochirus)], bullfrog tadpoles (Rana catesbeiana), and sediment were collected at both sites in Granite Creek in 2000. Crayfish, small fish, and tadpoles and were collected primarily with a Coffelt Mark 10 backpack electrofisher unit, seines, dipnets, and crayfish traps in Granite Creek and Watson Lake. Gill nets were also used to collect small fish in Watson Lake. Largemouth bass (Micropterus salmoides) were collected via Coffelt VVP-15 boat electrofisher at Watson Lake and Lynx Lake. Immediately after collection, samples were weighed and measured. Arizona Game and Fish Department helped electroshock largemouth bass in both Watson Lake and Lynx Lake during the summer of 2001. Whole body bass were wrapped in aluminum foil and placed on wet ice until they were transferred to a commercial freezer and stored until shipped for analysis. Depending on the size, similar sized taxa (green sunfish, golden shiner, crayfish) were composited and analyzed together. Adult bullfrogs were collected from Watson Lake in 2001 using a spotlight and gig.

Bullfrog tadpoles were composited from the downstream Granite Creek site (Site 2), while Watson Lake tadpoles were analyzed individually. Adult bullfrogs were collected at night from Watson Lake by gigging in August 2001. Individual frogs were bagged and placed on wet ice until returned to the office. Gastrointestinal tracts were removed from each frog, stomach contents visually inspected, and livers removed for individual analysis. The remainder of the adult frogs were weighed, wrapped in aluminum foil, and stored in a commercial freezer until they were shipped for analysis. Livers were also wrapped in aluminum foil and frozen. All samples were analyzed for trace elements.

Black phoebes were observed nesting under a bridge over Granite Creek in 2001. Four black phoebe eggs were collected, but only one was viable and analyzed. The edge of Watson Lake is dominated by bullrush and cattail. Thus, red-winged blackbird (*Agelaius phoeniceus*) nests were abundant in 2001. While collecting red-winged blackbird eggs, we discovered an American coot (*Fulica americana*) nest, and we collected one coot egg from the clutch of nine. We collected 11 red-winged blackbird eggs.

Collected eggs were placed on wet ice in the field and transferred to the lab. Eggs were weighed and then egg shell thickness was measured. Egg contents were weighed, placed in a chemically clean jar, and stored in a commercial freezer until analysis.

Sediment was collected in Granite Creek by collecting five subsamples at a site, then homogenizing them into one single composite sample per site. Approximately the top 10 centimeters (4 inches) of sediment was collected for each subsample. Spoonful-aliquots of the homogenous composite mixture were placed in trace element clean jars, weighed, sealed with a teflon-lined lid and placed on wet ice until the sample could be transferred to a commercial freezer and stored until they were shipped for analysis.

## Chemical analysis-

Fish, invertebrates, amphibians, eggs, and sediment were analyzed for aluminum, arsenic, barium, beryllium, boron, cadmium, copper, iron, lead, mercury, magnesium, manganese, nickel, selenium, strontium, vanadium, and zinc. Geological and Environmental Research Group (GERG), Texas A&M University, Texas analyzed metals from Granite Creek substrates in 2000 and Research Triangle Institute, Research Triangle Park, North Carolina analyzed metals from Watson and Lynx Lake in 2001. Organochlorine insecticides (OCs), total polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), dioxins and furans were analyzed in sediment, invertebrates, and fish, by GERG. Blanks, duplicates, and spiked samples were used to maintain laboratory quality assurance and quality control (QA/QC). QA/QC was monitored by Patuxent Analytical Control Facility (PACF). Analytical methodology and reports met or exceeded U.S. Fish and Wildlife Service (Service) QA/QC standards.

The tissue samples were extracted by the National Oceanic and Atmospheric Administration's (NOAA) Status and Trends Method (MacLeod et al. 1985) with minor revisions (Brooks et al. 1989; Wade et al. 1988). Briefly, the tissue samples were homogenized with a Teckmar Tissumizer. A 1 to 10-gram sample (wet weight) was extracted with the Teckmar Tissumizer by adding surrogate standards, Na<sub>2</sub>SO4, and methylene chloride in a centrifuge tube. The tissue extracts were purified by silica/alumina column chromatography to isolate the aliphatic and PAH/pesticide/PCB fractions. The PAH/pesticide/PCB fraction was further purified by HPLC in order to remove interfering lipids.

The quantitative analyses for all tissue PAHs, OCs, and total PCBs were performed by capillary gas chromatography (CGC) with a flame ionization detector for aliphatic hydrocarbons, CGC with electron capture detector for pesticides and PCBs, and a mass spectrometer detector in the SIM mode for aromatic hydrocarbons (Wade et al. 1988). There are specific cases where analytes requested for the pesticide and PCB analyses and are known to co-elute with other analytes in the normal CGC with electron capture. In these cases, the samples will be analyzed by CGC with a mass spectrometer detector in the SIM mode. Sediment samples were freeze-dried and extracted in a Soxhlet extraction apparatus, then analyzed as described above.

The lower limit of quantification (wet weight) was 0.25 ppb for most OCs, 2.5 ppb for toxaphene, 2.5 ppb PCBs, 2.5 ppb for PAHs, 0.005 ppb for most dioxins and furans, 0.001 ppbc for 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF), 0.01 ppb for octachlorodibenzodioxin (OCDD) and octachlorodibenzofuran (OCDF), and 10.0 ppb for PCP. Recovery in spiked samples ranged from 37.7% to 181% for OCs; 65% to 174% for total PCBs; 6.27% to 2815% for PAHs; 65% to 204% for dioxins and furans; 115% to 163% for TCDD and TCDF; 23.8% to 1943% ug/g for OCDD and OCDF; and 91.4% to 105% for PCP. All spiked samples fell within normal ranges. Quality Assurance/Quality Control and analytical results were approved by John Moore at Patuxent Analytical Control Facility. Organochlorine compounds are expressed in ug/g wet weight to facilitate comparing current residue levels with those reported in the literature. Because organochlorine residue levels were relatively low in sediment, crayfish, fish, and tadpoles collected in 2000, no samples were collected in 2001 for OC analysis.

PAHs that were analyzed include: 1-methylnaphthalene, 1-methylphenanthrene, 2-methyl naphthalene, C1-fluoranthenes and pyrenes, C1-phenanthrenes and anthracenes, C1-chrysenes, C1-dibenzothiophenes, C1-fluorenes, C1-naphthalenes, C2-phenanthrenes and anthracenes, C2-chrysenes, C2-fluorenes, C2-naphthalenes, C3-phenthenes and anthracenes, C3-chrysenes, C3-naphthalenes, C4-phenanthrenes and anthracenes, C4-chrysenes, acenaphthalene, acenaphthene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(g,h,i)perylene, benzo(k)fluoranthene, biphenyl, chrysene, dibenzo(a,h)anthracene, dibenzothiophene, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, perylene, phenanthrene, and pyrene.

Analysis of dioxin congeners included 1,2,3,4,6,7,8-heptachlorodibenzodioxin (HpCDD); 1,2,3,4,7,8-hexachlorodibenzodioxin; 1,2,3,6,7,8-hexachlorodibenzodioxin; 1,2,3,7,8,9-pentachlorodibenzodioxin (PeCDD); TCDD, and OCDD. Furan congeners included 1,2,3,4,6,7,8-heptachlorodibenzofuran; 1,2,3,4,7,8,9-heptachlorodibenzofuran; 1,2,3,4,7,8-hexachlorodibenzofuran; 1,2,3,6,7,8-hexachlorodibenzofuran; 2,3,4,6,7,8-hexachlorodibenzofuran; 1,2,3,7,8,-pentachlorodibenzofuran; TCDF, and OCDF. The 2,3,7,8-TCDD toxic equivalents (TEQ) were calculated for dioxins plus furans. For samples below the detection limit, one-half the detection limit of each sample was used to calculate the TEQ.

Mercury concentrations were quantified using cold vapor atomic absorption (USEPA 1984). All other elements were quantified by using inductively coupled plasma emission spectroscopy (Dahlquist and Knoll 1978; USEPA 1987). Metals recovery in spiked samples ranged from 76.2% to 127%. Chemical concentrations in sediment and some biota (Tables 2,3,5,6 and Appendices 1-6) are reported in ug/g (parts per million) dry weight to facilitate comparison of results with those of other studies and to avoid errors in interpretation associated with varying moisture levels in eggs and tissues (Stickel 1973). Chemical concentrations in Tables 4 and 7-10 and Appendices 7-10 are reported in ug/g wet weight. The lower limits of analytical quantification varied by element and are listed in Appendix 1.

Percent moisture is listed in Table 4 to facilitate wet weight to dry weight conversions. Wet weight values can be converted to dry weight equivalents by dividing the wet weight values by one minus percent moisture (as a decimal). This is illustrated by the following equation:

Dry Weight = Wet Weight

1 - Percent Moisture

Percent lipid is an important parameter in determining OC and total PCB exposures because these chemicals accumulate in adipose tissues.

We recognize that not all the elements listed in this report are "heavy metals" or even true metals. For the sake of convenience, and to avoid ambiguous terms such as "trace elements, metalloids, and heavy metals", we refer to all elements simply as metals.

Statewide background data on metals in Arizona soils was obtained by the U.S. Geological Survey (USGS) during a 14-year period from 1961 to 1975 (Earth Technology 1991). They analyzed 47 soil samples from various locations across the state to determine the concentration of selected metals. We compare our data against this state background data as well as human health guidelines in soil (ADEQ 2003) and aquatic wildlife thresholds (Persaud et al. 1993) in Table 2. We assumed that the Earth Technology (1991) and Arizona's (ADEQ 2003) soil data is comparable to the sediment that we collected.

Element concentrations in fish were compared with those reported in the National Contaminant Biomonitoring Program (NCBP) for fish collected in 1976-1984 from 117 stations nationwide (Table 4; Schmitt and Brumbaugh 1990). Concentrations of an element were considered elevated when they exceeded the 85<sup>th</sup> percentile of the nationwide geometric mean. The 85<sup>th</sup> percentile was not based on toxicity hazard to fish, but provided a frame of reference to identify element concentrations of potential concern.

#### Statistical analysis-

Relatively small numbers of sediments, fish, invertebrates, eggs, and amphibians were collected in 2000 and 2001. Contaminant concentrations were compared among species (n=9) and sampling locations (n=3) using a one-way analysis of variance (ANOVA). Samples across years were not combined, so we did not test for differences between years. Bonferroni t-tests were used for all pairwise comparisons to determine metal differences among species at Watson Lake. Largemouth bass contaminant concentrations collected from Watson Lake and Lynx Lake were compared using a one-way ANOVA. Data were log-transformed to common logarithms to improve homogeneity of variances, and geometric means (gmean) were calculated when residues were detected in more than 50% of the samples. When means were calculated, a value equal to one-half the lower limit of detection was assigned to any non-detected value prior to log-transformation. Retransformed geometric means are presented in the text and tables.

## **RESULTS**

A complete listing of all species and all sampling locations in 2000 and 2001 are listed below.

Table 1. Number and type of samples collected at Granite Greek and Watson and Lynx Lakes, Yavapai County, Arizona 2000 - 2001.

			Numbe	er of samples	s analyzed
Area	Sample	Tissue	Organo- chlorines	Metals	Dioxins/ furans/PAHs
Granite Creek					
Site 1	Sediment	NA	1	1	1
	Crayfish	whole body	2	2	2
	Green sunfish	whole body	2	2	2
	Golden shiner	whole body	2	2	2
	Black phoebe	eggs	0	1	0
Site 2	Sediment	NA	1	1	1
	Crayfish	whole body	2	2	2
	Bullfrog tadpoles	whole body	1	1	1
	Green sunfish	whole body	2	2	2
	Golden shiner	whole body	2	2	2
Watson Lake	Crayfish	whole body	0	9	0
	Bullfrog	whole body	0	9	0
	Bullfrog	liver	0	10	0
	Bullfrog tadpoles	whole body	0	10	0
	Bluegill sunfish	whole body	0	10	0
	Green sunfish	whole body	0	10	0
	Golden shiner	whole body	0	10	0
	Largemouth bass	whole body	0	6	0
	American coot	eggs	0	1	0
	Red-winged blackbird	eggs	0	11	0
Lynx Lake	Largemouth bass	whole body	0	5	0

## Metal concentrations—

Sediment: Sediments were collected at Site 1 and 2 near Southwest Forest Industries on Granite Creek in 2000. Elevated levels of arsenic, chromium, copper, and nickel were

recovered (Table 2). Arsenic was present at Site 1 above the Arizona mean background concentrations in soil, human health guidelines for soil, and the lowest effect aquatic wildlife threshold. Chromium and copper were 1.5-times and 1.17-times greater than the lowest effect aquatic wildlife threshold, respectively. For both Site 1 and 2, nickel was higher than the Arizona mean background concentration as well as the lowest effect aquatic wildlife threshold.

Table 2. Priority pollutants in soil/sediment (ppm dry weight): Arizona background levels (soil), human health guidelines (soil), aquatic wildlife toxicity thresholds (sediment), and Granite Creek sediment.

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		izona kground <sup>i</sup>		n Health lelines <sup>2</sup>	Aquatic \ Thresh		Grani	te Creek <sup>4</sup>
Element	Mean	Maximum	Residential	Non-resident	Lowest effect	Severe effect	Site 1	Site 2
Aluminum	55,213	100,000	77,000	1,000,000	NA <sup>5</sup>	NA	8670	6402
Arsenic	9.8	97.	10.	10.	6.0	33.	13.0	5.37
Barium	565	1,500	5,300	110,000	NA	NA	105	73.4
Beryllium	0.52	5.	1.4	11.0	NA	NA	0.48	0.38
Cadmium	NA	NA	38	850	0.6	10.	< 2.00	< 2.00
Chromium	61.3	300.	2,100	4,500	26.	110.	33.8	21.4
Copper	30.	200.	2,800	63,000	16.	110.	<b>18.</b> 7	12.4
Lead	23.4	100.	400	2.000	31.	250.	11.8	11.3
Mercury	0.10	0.57	6.7	180	0.2	2.0	< 0.20	< 0.20
Molybdenum	3.0	3.3	380	8,500	NA	NA	< 2.00	< 2.00
Nickel	27.5	150.	1,500	34,000	16.	75.	43.4	26.6
Selenium	0.30	1.6	380	8,500	NA	NA	<1.00	<1.00
Vanadium	71.3	300.	540	12,000	NA	NA	28.6	20.1
Zinc	62.1	150.	23,000	510,000	120.	820.	50.6	31.4

<sup>&</sup>lt;sup>1</sup>Data from Earth Technology (1991).

Crayfish: We focused our presentation of metals on arsenic, chromium, copper, mercury and selenium (Table 3), although all metals data are presented in Appendix 2. Geometric means (gmeans) and ranges were calculated for composite crayfish samples at both Granite Creek sites and Watson Lake. Only the Watson Lake crayfish had a large enough sample size to calculate geometric mean. The gmeans were 0.46, 1.94, 39.02, 0.10, and 1.63 ppm, dry weight, for arsenic, chromium, copper, mercury, and selenium, respectively. Arsenic was detected in 8 out of 13 crayfish samples. Copper was detected in all crayfish samples.

<sup>&</sup>lt;sup>2</sup>Residential and non-residential standards data from Arizona Department of Environmental Quality. Title 18. Environmental Quality, Chapter 7. Remedial Action. Article 2. Soil Remediation Standards.

<sup>&</sup>lt;sup>3</sup>Data from Persaud et al. (1993).

<sup>&</sup>lt;sup>4</sup>Granite Creek data in bold italics indicates that sediment concentrations exceed either or both the non-residential human health guidelines or the lowest aquatic wildlife toxic threshold.

<sup>&</sup>lt;sup>5</sup> NA = Not available.

Chromium was detected in 10 out of 13 crayfish samples. Mercury was detected in 10 out of 13 crayfish samples. Selenium was detected in 9 out of 13 crayfish samples.

Table 3. Geometric mean arsenic, copper, chromium, mercury, and selenium concentrations (ppm dry weight) in crayfish and bullfrogs collected from Granite Creek (Sites 1 and 2) and Watson Lake (Site 3), Yavapai County, Arizona, 2000-2001.

	_				Geometric	mean (range) n <sup>1</sup>		
Sample	Tissue	Site	$N^2$	Arsenic	Copper	Chromium	Mercury	Selenium
Crayfish	Whole body	3	9	0.46 (ND <sup>3</sup> - 1.80)	39.02 (25.6 - 51.1) 9	1.94 (ND - 22.5)	0.10 (0.05 - 0.18) <i>9</i>	1.63 (1.05 - 2.26) 9
Crayfish	Whole body	1	2	(2.91 - 3.06) 2	(47.2 - 64.0) 2	(16.3 - 16.5) 2	(ND - 0.22)	(ND) 0
Crayfish	Whole body	2	2	(1.47 - 4.42) 2	(32.3 - 43.1)	(14.7 - 15.7) 2	(ND) 0	(ND) 0
Bullfrog tadpoles	Whole body	3	11	1.37 (0.99 - 3.92) 4	9.26 (7.03 - 20.4) 11	19.19 (5.71 - 84.20) 11	0.06 (0.025 - 0.11) 10	(ND - 1.26)
Bullfrog tadpoles	Whole body	2	1	(4.82) 1	(15.6) 1	(17.0) 1	(ND) 0	(0.57) 1
Bullfrog (adult)	Liver	3	10	0.34 (0.23 - 0.96) 3	30.83 (4.76 - 164.) 10	0.29 (0.25 - 0.49) 2	0.62 (0.13 - 2.38) 10	1.82 (0.54 - 5.22) 10
Bullfrog (adult)	CR⁴	3	9	1.37 (0.25 - 20.70) 8	2.78 (1.69 - 5.07) 9	14.10 (0.54 - 64.60) <i>9</i>	0.38 (0.15 - 0.64) <i>9</i>	1.14 (0.25 - 2.30) <i>9</i>

 $<sup>^{1}</sup>n =$  Number of samples with detectable concentrations.

Bullfrogs: Bullfrog tadpoles were collected from Sites 2 and 3. Tadpole sample sizes were only large enough from Watson Lake to calculate gmeans. The geometric mean was 1.37 ppm dry weight for arsenic and 19.19 ppm dry weight for chromium. The gmean copper concentration in tadpoles was 9.26 ppm dry weight and mercury was 0.06 ppm dry weight. Selenium was only detected in two tadpole samples. Therefore, there is no gmean for selenium in bullfrog tadpoles. In adult bullfrogs, liver concentrations of copper, mercury, and selenium were all higher than the remainder of the carcass. The gmean for copper in the adult bullfrog was 11-times greater in the liver than in the rest of the body. Mercury and selenium gmeans were both 1.6-times greater in the liver than in the carcass remainder. Low concentrations of arsenic and chromium were detected in adult bullfrogs livers. Carcass remainder concentrations were 1.37 ppm dry weight arsenic and 14.1 ppm dry weight chromium.

 $<sup>^{2}</sup>$  N = Number of samples analyzed.

 $<sup>^{3}</sup>$  ND = Not detected.

<sup>&</sup>lt;sup>4</sup>CR = Carcass Remainder = whole frog minus liver and gastrointestinal tract.

Fish: Metal concentrations in one fish sample from Lynx Lake were dramatically lower than the rest of the Lynx Lake largemouth bass samples. We decided to include this fish in the data analysis since this sample was analyzed twice and duplicate concentrations were the same or very similar to the original data.

Mean concentrations of seven elements in fish collected from Granite Creek, Watson Lake, and Lynx Lake are compared in Table 4 to the NCBP 85<sup>th</sup> percentile (Schmitt and Brumbaugh 1990). The moisture content of these fish samples are presented in Table 4 because the NCBP data are in wet weight and we converted our dry weight values (Appendices 4 and 5) to wet weight for comparison. Mean concentrations of arsenic, cadmium, copper, mercury, and zinc were higher than the NCBP 85<sup>th</sup> percentile.

Mean arsenic concentrations of 0.78 to 0.79 ppm in both green sunfish and golden shiners from Granite Creek were elevated over the NCBP's 85<sup>th</sup> percentile of 0.27 ppm. Arsenic was greater in Granite Creek green sunfish (0.78 ppm wet weight) than in Watson Lake green sunfish (0.15 ppm wet weight). Similarly, there was 0.79 ppm wet weight arsenic in Granite Creek golden shiners and only 0.20 ppm wet weight arsenic in Watson Lake golden shiners.

Only one site had a big enough sample size to calculate a mean cadmium concentration of 0.07 ppm for largemouth bass, which is greater than the NCBP concentration of 0.05 ppm.

The NCBP did not report an 85<sup>th</sup> percentile for chromium in fish. Watson Lake green sunfish had 9.71 ppm wet weight chromium versus 1.98 ppm wet weight chromium in Granite Creek green sunfish. Chromium is almost 5-times higher in Watson Lake green sunfish than in Granite Creek green sunfish. The same trend is observed between golden shiners in Watson Lake and Granite Creek. Chromium is almost 8-times greater in Watson Lake golden shiners (16.64 ppm) than in Granite Creek (2.19 ppm). Despite their phylogenetic similarity, bluegill sunfish had a lower chromium concentration in Watson Lake (2.45 ppm) than Watson Lake green sunfish (9.71 ppm). Largemouth bass were sampled in Lynx Lake as a comparison, but Lynx Lake bass had twice as much chromium (26.26 ppm) compared with Watson Lake largemouth bass (12.62 ppm).

The highest mean copper concentrations were 3.60 and 3.35 ppm from green sunfish and golden shiners, respectively, in Granite Creek. Watson Lake golden shiners and largemouth bass also had elevated mean copper concentrations (1.30 and 1.19 ppm, respectively). Golden shiners in Granite Creek had a copper concentration 2.6-times greater than the golden shiners in Watson Lake. Watson Lake largemouth bass had 1.19 ppm copper body residues which was similar to the 1.57 ppm copper in Lynx Lake largemouth bass. All copper values exceeded the NCBP 85<sup>th</sup> percentile for copper, which is 1.0 ppm.

The comparison between copper in bluegill sunfish and green sunfish from Watson Lake is opposite that for chromium. Bluegill have higher concentrations of copper (0.76 ppm) than green sunfish (0.15 ppm).

Mean mercury concentrations in Granite Creek golden shiners were the highest of all fish sampled: 4.6-times the NCBP 85<sup>th</sup> percentile of 0.17 ppm. Granite Creek green sunfish and Watson Lake largemouth bass were also elevated above 0.17 ppm mercury, 2.6-times and 1.9-times, respectively.

Although no fish from Granite Creek or Watson Lake had selenium levels higher than the NCBP 85<sup>th</sup> percentile, similarities exist among selenium concentrations in Watson Lake bluegill and green sunfish (0.21 and 0.26 ppm, respectively). Largemouth bass in Watson Lake and Lynx Lake both had selenium concentrations of 0.48 ppm.

Three mean zinc concentrations exceeded the NCBP threshold of 34.2 ppm. These include 109 ppm for Granite Creek green sunfish, 207 ppm for Granite Creek golden shiners, and 57.8 ppm for Watson Lake golden shiners. Again, golden shiners in Granite Creek had a 3.6-times higher level of zinc than Watson Lake golden shiners. Granite Creek green sunfish had a 3.7-times higher concentration of zinc than Watson Lake green sunfish.

Table 4. Arithmetic mean concentrations of seven elements in fish collected from Granite Creek, Watson Lake, and Lynx Lake compared to the National Contaminant Biomonitoring Program 85<sup>th</sup> percentile, 2000.<sup>1</sup>

P	, 2000.			Arith	metic mean.	ppm wet we	ight (n) <sup>2</sup> / r	ange		
Species  NCBP 85th	Location U.S.	N³ 109	Arsenic 0.27	Cadmium 0.05	Copper 1.0	Chromium	Mercury 0.17	Selenium 0.73	Zinc 34.2	Moist (%) NA <sup>4</sup>
Green sunfish	Granite Creek	4	0.78 (4) 0.59 - 1.10	(0)	3.60 (4) 3.23 - 4.61	1.98 (4) 1.51 - 2.35	0.45 (4) 0.31 - 0.73	(0)	109 (4) 83.1 - 149.	77.8
Golden shiner	Granite Creek	4	0.79 (4) 0.66 - 0.89	(0)	3.35 (4) 2.89 - 3.83	2.19 (4) 1.92 - 2.43	0.78 (4) 0.62 - 0.92	(0)	207 (4) 177 270.	77.3
Green sunfish	Watson Lake	10	0.15 (5) ND <sup>5</sup> - 0.41	(0)	0.15 (10) 0.36 - 0.96	9.71 (10) 4.09 - 29.85	0.12 (10) 0.05 - 0.35	0.26 (10) 0.12 - 0.44	29.3 (10) 22.7 - 38.8	74.9
Bluegill sunfish	Watson Lake	10	(0)	(0)	0.76 (10) 0.56 - 1.57	2.45 (10) 0.20 - 13.83	0.07 (10) 0.06 - 0.08	0.21 (7) ND - 0.41	28.2 (10) 24.5 - 31.2	
Golden shiner	Watson Lake	10	0.20 (8) ND - 0.38	(1) ND - 0.06	1.30 (10) 0.83 - 2.00	16.64 (10) 6.78 - 33.13	` ′	0.33 (10) 0.15 - 0.44	57.8 (10) 49.1 - 67.0	
Large- mouth bass	Watson Lake	6	(2) ND - 0.33	(0)	1.19 (6) 0.88 - 1.09	12.62 (6) 4.09 - 24.16	0.33 (6) 0.20 - 0.72	0.48 (6) 0.39 - 0.68	24.7 (6) 18.1 - 40.9	60.3
Large- mouth bass	Lynx Lake	5	(1) ND - 0.26	0.07 (4) ND - 0.15	1.57 (5) 0.59 - 3.96	26.26 (5) 0.43 - 37.39	0.09 (5) 0.04 - 0.17	0.48 (5) 0.31 - 0.66	29.1 (5) 18.2 - 48.5	56.6

<sup>&</sup>lt;sup>1</sup> NCBP data from Schmitt and Brumbaugh (1990). Although lead was reported in NCBP samples ( 85<sup>th</sup> percentile = 0.22 ppm), lead was not detected in fish from Watson or Lynx Lakes.

<sup>&</sup>lt;sup>2</sup>n = Number of samples with detectable concentrations.

 $<sup>^{3}</sup>N = Number of samples analyzed.$ 

<sup>&</sup>lt;sup>4</sup>NA = Not available.

<sup>&</sup>lt;sup>5</sup>ND = Not detected.

The geometric means of arsenic, chromium, copper, mercury, and selenium in fish from Watson Lake are compared in Table 5. There were no statistical differences among fishes arsenic gmean concentrations. Arsenic gmeans ranged from a low of 0.07 ppm dry weight in bluegill sunfish and largemouth bass to a high of 0.40 ppm dry weight in golden shiners. Green sunfish had a significantly lower chromium gmean (3.42 ppm dry weight) compared to the other three species of fish sampled (P < 0.0001). The greatest difference in chromium was in golden shiners, with a chromium gmean of 55.9 ppm dry weight. Copper concentrations were not statistically different for bluegill sunfish, green sunfish, and largemouth bass. Golden shiners accumulated significantly more copper than the other species (4.64 ppm dry weight, P < 0.05). Mercury concentrations in bluegill sunfish and green sunfish were similar to each other, but were significantly lower than the mercury burdens in golden shiners and largemouth bass (P < 0.05). Bluegill sunfish and largemouth bass selenium concentrations were statistically different from one another (0.61 ppm dry weight vs. 1.30 ppm dry weight, P < 0.05), but green sunfish and golden shiner selenium concentrations were similar to both the bluegill sunfish and the largemouth bass concentrations (Table 5).

Table 5. Geometric mean concentrations (ppm dry weight) of arsenic, copper, mercury, and selenium in fish collected from Watson Lake, 2000-2001.

			Ge	ometric mean (rang	ge) $n^1$	
Species	$N^2$	Arsenic	Chromium	Copper	Mercury	Selenium
Bluegill sunfish	10	$0.07$ $(ND^3 - 1.89)$ $3 A^4$	29.5 (14.2 - 99.50) 10 A	2.58 (1.85 - 5.23) 10 A	0.24 (0.21 - 0.27) 10 A	0.61 (ND - 1.44) 7 A
Green sunfish	10	0.15 (ND -1.70) 4 A	3.41 (0.74 - 53.4) 10 B	1.90 (1.48 - 3.69) 10 A	0.37 (0.20 - 1.26) 10 A	0.89 (ND -1.68) 9 AB
Golden shiner	10	0.40 (ND -1.53) 8 A	55.9 (25.5 - 125.0) 10 A	4.64 (3.33 - 7.54) 10 B	0.60 (0.46 - 0.76) 10 B	1.15 (0.57 - 2.16) 10 AB
Largemo uth bass	6	0.07 (ND - 0.86) 2 A	26.4 (6.99 - 57.8) 6 A	2.90 (1.61 - 4.56) 6 A	0.76 (0.57 - 1.23) 6 B	1.30 (1.15 - 1.45) 6 B

<sup>&</sup>lt;sup>1</sup>n = Number of samples with detectable concentrations.

Arsenic level of significance for differences among species was P = 0.14

Copper level of significance for differences among species was P<0.0001
Chromium level of significance for differences among species was P<0.0001

Mercury level of significance for differences among species was P<0.0001
Selenium level of significance for differences among species was P = 0.021

One-way analysis of variance (Table 6) revealed that gmean arsenic, chromium, copper and selenium concentrations were not significantly different in largemouth bass at Watson Lake

 $<sup>^{2}</sup>N = Number of samples analyzed.$ 

 $<sup>^{3}</sup>ND = Not detected.$ 

<sup>&</sup>lt;sup>4</sup>For each element, means sharing the same letter are not statistically different.

and Lynx Lake (P = 0.71 arsenic; P = 0.82 chromium; P = 0.9438 copper; and P = 0.2217 selenium). The Watson Lake gmean mercury concentration in largemouth bass (0.76 ppm dry weight) was significantly greater than Lynx Lake largemouth bass (0.19 ppm dry weight; P < 0.0001).

Table 6. Geometric mean concentrations (ppm dry weight) of arsenic, copper, chromium, mercury, and selenium in largemouth bass collected from Watson Lake and Lynx Lake.

				· · · · · · · · · · · · · · · · · · ·		
		Geome	etric mean (ra	nge) $n^1$		
				Element		
Location	$N^2$	Arsenic	Copper	Chromium	Mercury	Selenium
Watson Lake	6	0.075 (ND <sup>3</sup> - 0.86) 2 A <sup>4</sup>	2.90 (1.61 - 4.56) 6 A	26.40 (6.99 - 57.8) 5 A	0.76 (0.57-1.23) 6 A	1.30 (1.16 - 1.45) 6 A
Lynx Lake	5	0.051 (ND - 0.85) I A	2.98 (0.93 -5.03) 5 A	32.88 (0.71 - 123.0) 5 A	0.19 (0.14 - 0.28) 5 B	1.10 (0.89 - 1.86) 5 A

<sup>&</sup>lt;sup>1</sup>n = Number of samples with detectable concentrations.

Arsenic level of significance for differences between lakes was P=0.71 Chromium level of significance for differences between lakes was P=0.82 Copper level of significance for differences between lakes was P=0.94 Mercury level of significance for differences between lakes was P<0.0001 Selenium level of significance for differences

between lakes was P=0.22

Birds: The gmean copper concentration in red-winged blackbird eggs was 2.60 ppm dry weight. The gmean mercury concentration in red-winged blackbird eggs was 0.45 ppm dry weight. The gmean selenium concentration in red-winged blackbird eggs was 1.43 ppm dry weight. Because we were only able to collect one American coot egg and one black phoebe egg, results of metal concentrations are presented in Appendix 7.

## *Organochlorine residues*–

Sediment: Low concentrations of chlorinated organic compounds were detected in Sites 1 and 2 sediments below Southwest Forest Industries on Granite Creek. Total PCBs were the only organochlorine compound (Table 7) detected in sediment at 0.010-0.011 ppm wet weight. The p,p'-DDE concentration at both sampling sites in Granite Creek was at least 2 orders of magnitude lower than the threshold effects level for freshwater sediment in NOAAs Screening Quick Reference Tables (SQuiRTs) (Buchman 1999). The concentration of total PCBs in Granite Creek, about 0.01 ppm wet weight, was at least 4 orders of magnitude lower

 $<sup>^{2}</sup>N =$  Number of samples analyzed.

 $<sup>^{3}</sup>ND = Not detected.$ 

<sup>&</sup>lt;sup>4</sup>For each element, means sharing the same letter are statistically similar.

than the consensus-based probable effect concentration (Ingersoll et al. 2000). Transnonachlor sediment concentrations ranged from 0.26 - 0.56 ppb wet weight.

Table 7. Organochlorine insecticides and PCBs (ppm wet weight) in sediment, crayfish, and fish collected from two locations in Granite Creek (Sites 1 and 2), Arizona, 2000.

	Sed	liment <sup>2</sup>	Cra	ayfish³	Green	n sunfish³	Gold	len shiner <sup>3</sup>
Compound <sup>1</sup>	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
p,p'-DDE	0.00019	0.00020	0.0032	0.0013	0.0088	0.010	0.012	0.012
trans-nonachlor	0.00026	0.00056	0.0030	0.0021	0.0083	0.016	0.0071	0.0077
Total PCB	0.010 0.011		0.026	0.010	0.063	0.068	0.051	0.041

<sup>&</sup>lt;sup>1</sup>No other organochlorine compounds were detected.

Crayfish: Crayfish concentrations from Sites 1 and 2 on Granite Creek were 0.0032 and 0.0013 ppm wet weight for DDE and 0.026 and 0.010 ppm wet weight. Total PCBs were detected in the Site 1 at 0.03 ppm wet weight and Site 2 at 0.01 ppm wet weight.

Fish: Organochlorines were detected in all green sunfish collected. Concentrations were low; around 0.01 ppm wet weight p,p'-DDE was detected in both Sites 1 and 2 in Granite Creek. Trans-nonachlor in green sunfish ranged from 0.063 to 0.068 ppm wet weight. Total PCBs were detected from 0.0083 to 0.0016 ppm wet weight in green sunfish. Organochlorines were detected at 0.012 ppm wet weight p,p'-DDE, 0.071 - 0.077 ppm wet weight trans-nonachlor, and from 0.051 to 0.041 ppm wet weight total PCBs in golden shiners.

Appendix 8 lists p,p'-DDE, trans-nonachlor, and total PCBs found in sediment, crayfish, green sunfish, golden shiners, and bullfrog tadpoles. Also included are the moisture and lipid content of these samples.

#### PAHs and PCP-

Sediment: Polyaromatic hydrocarbons were analyzed in sediment collected from Sites 1 and 2. In general, PAH concentrations were greater in sediments than in crayfish or fish (Appendix 1). Elevated concentrations of benzo(a)anthracene (92.2 - 117 ppb wet weight), C1-fluoranthenes and pyrenes (29.5 - 46.6 ppb wet weight), benzo(a)pyrene (151 - 222 ppb), benzo(b)fluoranthene (121-173 ppb), benzo(e)pyrene (66 - 102 ppb), benzo(g,h,i)perylene (84 - 128 ppb), benzo(k)fluoranthene (36.8 - 48.3 ppb), chrysene (103 - 162 ppb), fluoranthene (182 - 281 ppb), indeno(1,2,3-c,d)pyrene (90.3 - 141 ppb), phenanthrene (114 - 176 ppb), and pyrene (172 - 260 ppb) were found in Granite Creek. Site 2 PAH sediment concentrations were generally less than the Site 1 sediment concentrations. Pentachlorophenol and pentachloro-anisole are also listed in Appendix 1. Pentachloro-anisole is a derivative of PCP. Pentachlorophenol ranged from 5.44 ppb wet weight in Site 2

<sup>&</sup>lt;sup>2</sup>One sample was collected at each location.

<sup>&</sup>lt;sup>3</sup>Two samples were collected at each location. Data points represent an average of the two readings.

to 21.2 ppb wet weight upstream. Pentachloro-anisole was only detected in the Site 1 at 0.18 ppb wet weight.

Crayfish: Crayfish PAH concentrations never exceeded 20.9 ppb wet weight (acenaphthene). The highest PAH concentrations were detected at Site 1 crayfish samples. Most PAHs in crayfish were below the reported detection limit of 2.47 ppb wet weight. Of those samples with detectable PAH concentrations, the range of concentrations was from 2.48 to 20.9 ppb wet weight. While the parent compound PCP was not detected in crayfish, the Site 1 crayfish sample had a burden of 0.50 ppb wet weight pentachloro-anisole.

Fish: Polyaromatic hydrocarbons in fish samples ranged from 2.54 - 32.1 ppb wet weight in green sunfish and from 2.46 - 80.1 ppb wet weight in golden shiners. Acenaphthene concentrations were highest in green sunfish and golden shiners. The trend in fish was similar to that seen in sediments and crayfish: Site 1 PAH concentrations were generally higher than the Site 2 concentrations.

Pentachloropenol was not detected in either green sunfish or golden shiners at the Granite Creek upstream site. At Site 2, PCP was not detected in golden shiners, but was detected at 32.2 ppb wet weight in green sunfish. Higher concentrations of pentachloro-anisole were observed in greater quantities at Site 1 (2.26 - 3.42 ppb wet weight), in green sunfish and golden shiners, respectively, than at Site 2 (1.23 - 2.02 ppb wet weight). Although the highest PCP concentration was in one composite sample of green sunfish from Site 2, fish composites from both sites had pentachloro-anisole burdens from Granite Creek. These pentachloro-anisole concentrations in fish could be from residual contamination from the wood-preservation company.

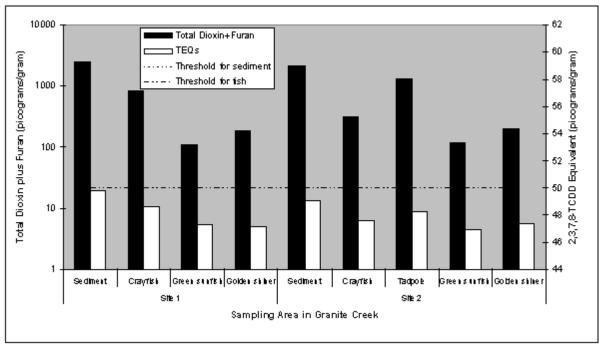
## Dioxins and furans-

Sediment: A compilation of dioxin and furan data in sediment, invertebrate, and fish collected from Granite Creek and Watson Lake is presented in Appendices 10 and 11. All dioxins and furans were detected in sediment samples from Sites 1 and 2 except for PeCDD and 1,2,3,4,7,8-HxCDF at the Site 2 sediment and PCDF and TCDF at Sites 1 and 2. The most abundant congeners in sediment were OCDD and HpCDD. Buchman (1999) determined in the NOAA SQuiRTs that the upper effects threshold for TCDD is 0.0088 ppb dry weight from a *Hyallela azteca* sediment toxicity test. The TCDD sediment concentrations in Granite Creek were 0.0005 ppb dry weight (Sites 1 and 2). Both of these concentrations are below the SQuiRT upper effects threshold level of 0.0088 ppb dry weight in sediments.

Also, as a reference, we used TEQs to interpret the sediment concentrations analyzed in our study since it is the most toxic dioxin congener. All other congeners toxicity is scaled to that of TCDD, which makes comparison of potential toxicity easier. Sediment TEQs ranged from 19.20 ppt dry weight at Site 2 to 24.92 ppt dry weight at Site 1. Next, we compared the

sum of dioxin and furan concentrations among samples to TEQs (Figure 2) against EPA's recommended threshold levels of 60 ppt TEQ wet weight in sediments and 50 ppt wet weight TEQ in fish tissue. EPA has determined a low risk fish threshold concentration of 60 pg/g (ppt) TCDD (USEPA 1993). None of the sediment TEQs were greater than EPA's threshold level of 60 ppt TEQ wet weight (Figure 2).

Figure 2. 2,3,7,8-TCDD fish and sediment TEQs compared to summed total of dioxins and furans in different media for Sites 1 and 2 in Granite Creek, Arizona, 2000.



TCDD is the most toxic dioxin, but only 0.02% 2,3,7,8-TCDD was detected from all the congeners in sediment. The proportionally small amount of TCDD in sediment at Granite Creek explains why the TEQs fall well below the 60 ppt TEQ wet weight threshold as well as why the total dioxin and furan concentrations were comparatively so great. All total dioxin and furan concentrations were 1 - 2 orders of magnitude greater than the TEQ concentrations because the most abundant congeners were not the most toxic. Total dioxin plus furans in sediments were 100 times greater than the corresponding TEQs.

Crayfish: Dioxins and furans were detected in the Granite Creek crayfish samples. The most abundant congeners in crayfish were OCDD and HpCDD. TEQs in crayfish ranged from 9.19 to 12.19 ppt wet weight at Site 1 to 5.27 to 7.33 ppt wet weight at Site 2. The greatest TEQ of all the biotic samples was 12.19 ppt wet weight in crayfish at Site 1. The 2,3,7,8-TCDD was not abundant in crayfish samples. Therefore, the total dioxin plus furan concentration in crayfish was 100 times greater than the crayfish TEQs.

Tadpole: Although only one tadpole composite sample was analyzed for dioxins and furans, it is interesting to note that the total dioxin and furan concentration in tadpoles was closer to the sediment concentration than to the other biotic samples. There is no threshold level for TEQs in tadpoles. However, the TEQ in tadpoles at Site 2 was 9.0 ppt wet weight. This is below the fish TEQ threshold of 50 ppt wet weight. The greatest amount of dioxins and furans detected in the tadpole sample was 76% OCDD. The 2,3,7,8-TCDD was detected in 0.037% of the sample.

Fish: The only dioxin detected in Granite Creek fish samples was 1,2,3,4,6,7,8-HpCDD. Two furans were detected in fish samples, 1,2,3,4,6,7,8-HpCDF and 1,2,3,7,8-PeCDF. The threshold for low risk to a predatory fish is <50 pg/g (ppt) wet weight. TEQs ranged from 3.28 ppt wet weight in green sunfish collected at Site 2 to 6.18 ppt wet weight in golden shiners collected at Site 2. The range of TEQs from Site 1 was 4.79 - 5.89 ppt wet weight. Fish TEQs were well below the 50 ppt threshold level for effects to predatory fish. The 2,3,7,8-TCDD composed between 0.15 - 0.62% of the total amount of congeners in Granite Creek. The most abundant congeners detected in fish samples ranged from 16 - 66% OCDD and from 10 - 55% 1,2,3,4,6,7,8-HpCDF. Because less toxic congeners comprised most of the dioxins and furans detected in fish samples, the total dioxin and furan concentration was 10-times greater in fish than the TEQ concentrations (Figure 2).

## **DISCUSSION**

#### Metal concentrations—

Sediment: Granite Creek Site 1 sediment concentrations of arsenic, chromium, copper, and nickel exceeded lowest effect aquatic wildlife thresholds (Persaud et al. 1993). Given the history of the Southwest Forest Industries Superfund Site, the elevated levels of arsenic, chromium, and copper are not unexpected. Further downstream in Granite Creek, nickel is the only trace metal that still remains higher than the lowest effect aquatic wildlife threshold. A variety of metals are used in the wood treatment industry. Although Southwest Forest Industries primarily used PCP, it is possible that elevated nickel concentrations in Granite Creek sediment remain from this operation. It is also possible that elevated sediment nickel concentrations are remnant from other dischargers into Granite Creek, such as the Sundog Ranch Road Wastewater Treatment Plant for the City of Prescott or the VA (Figure 1). Sediment concentrations elevated above the lowest effect aquatic wildlife threshold pose a risk to ecological receptors in Granite Creek. However, the Granite Creek sediment nickel concentration was the only trace metal close to the consensus based probable effect concentration (PECs; MacDonald et al. 2000; Ingersoll et al. 2000) at which harmful effects are likely to be observed due to sediment exposure. Possible harmful effects due to elevated sediment nickel concentrations include decreased growth and survival and reproduction of benthic invertebrates and/or fishes in Granite Creek.

Crayfish: The highest arsenic concentration in crayfish was 4.42 ppm dry weight at Site 2. This concentration is less than the 5.37 to 13.0 ppm dry weight arsenic range for Granite Creek sediment. Crayfish are not bioaccumulating arsenic in Granite Creek.

The greatest crayfish copper concentration was 64.0 ppm dry weight, which is 3.4-times greater than the highest copper sediment concentration. Although copper in Granite Creek is not greatly elevated over the lowest effect aquatic wildlife threshold for sediment, it appears that crayfish are preferentially accumulating copper in Granite Creek. This may be due to the close association of crayfish and streambeds. Crayfish continually resuspend stream sediments and burrow into stream banks. While on the bottom of the creek, crayfish move water over their gills to breathe. Crayfish may be exposed to copper in Granite Creek from water and sediment, both while breathing, eating, and creating shelter. Also, aquatic mollusks and arthropods with hemocyanin typically have elevated levels of copper over the surrounding media (Neff and Anderson 1977). Copper in crayfish from this study fall within reported copper values in field collections of other crayfish species (Eisler 1998).

The highest chromium concentration in crayfish, 22.5 ppm dry weight from Watson Lake, corresponds with the chromium sediment concentration range of 21.4 to 33.8 ppm dry weight. Crayfish appear to be accumulating chromium consistent to sediment concentrations. As long as chromium is in this drainage, crayfish are likely to continue to have chromium burdens. The ecological significance of elevated chromium in crayfish tissues is unknown.

The greatest mercury concentration in crayfish was 0.22 ppm dry weight at Site 1, but mercury was not detected in Granite Creek sediments. Mercury easily bioaccumulates within an aquatic environment and is apparently bioaccumulating in crayfish here. Northern crayfish mercury concentrations were also studied in Canada (Jenkins 1980). Crayfish from the central Canadian location ranged from 0.09 - 0.49 ppm mercury wet weight. For comparison, crayfish mercury concentrations in Watson Lake ranged from 0.01 - 0.09 ppm wet weight and one Site 1 crayfish sample in Granite Creek had 0.05 ppm wet weight mercury. All of these samples fall within the crayfish mercury range from central Canada and well below Jenkins (1980) contaminated site crayfish with 1.4 - 7.4 ppm wet weight mercury. It is also not known definitively if the superfund site is the source of the mercury. Mercury is deposited worldwide into aquatic environments from the air. Other possible sources of mercury include the wastewater treatment plant, the VA, and the town of Prescott.

Similar to mercury, selenium was not detected in Granite Creek sediments, but was detected as high as 2.26 ppm dry weight in crayfish from Watson Lake. Selenium also bioaccumulates in aquatic environments. Selenium is naturally occurring in Arizona bedrock, which could be the source of the selenium. Selenium threshold values for crayfish do not exist, but the recommended national tissue-based criterion for selenium is 4 ppm (Hamilton 2002). Using the selenium gmean of 1.63 ppm dry weight, our samples are 2.5-times below the proposed criterion.

In summary, crayfish appear to be bioaccumulating mercury and selenium in the Granite Creek drainage below the superfund site. Crayfish mercury concentrations are equivalent to reference concentrations at other sites and crayfish selenium concentrations are still below adverse effects thresholds. While crayfish copper concentrations are elevated over the Granite Creek sediment, crayfish blood contains hemocyanin, a respiratory pigment made with copper. Arsenic and chromium concentrations in crayfish are equivalent to or less than sediment concentrations.

Bullfrogs: Bullfrog tadpole and carcass arsenic gmeans from Watson Lake were the same (1.37 ppm dry weight). Most bullfrog samples had higher arsenic concentrations than crayfish and either lower or equivalent concentrations with sediment from Granite Creek. The arsenic concentration in tadpoles exposed to coal fly ash in an ash basin settling pond was 25.95 - 48.0 ppm dry weight (Rowe et al. 1998; Rowe et al. 1996). These tadpoles exhibited oral deformities, axial malformations, and increased metabolic rates (Hopkins et al. 2000). Using this study as a comparison, the Granite Creek and Watson Lake tadpoles are not likely to develop abnormalities or adverse effects from the arsenic concentrations.

Copper and chromium concentrations decreased from 9.26 ppm dry weight copper and 19.19 ppm dry weight chromium in bullfrog tadpoles to 2.78 ppm dry weight copper and 14.10 ppm dry weight chromium in adult bullfrog. Dietary changes during bullfrog metamorphosis may account for the decrease in copper and chromium concentrations in adult bullfrogs. Bullfrogs remain tadpoles for 1 to 2 years and are herbivorous during this time. After metamorphosis, adult bullfrogs become carnivorous. Adult bullfrogs are not in as much contact with sediments as tadpoles and breathe atmospheric oxygen, unlike tadpoles. Because of these reasons, we would expect to see lower metal concentrations in adults than in tadpoles. To examine copper and chromium toxicity, the ash basin studies again provide good data for comparison. Ash basin tadpoles had between 31.4 - 116 ppm dry weight copper and 17.2 -27.25 ppm dry weight chromium (Rowe et al. 1996; Hopkins et al. 2000). Given that the tadpole gme ans for copper and chromium were 9.26 and 19.19 ppm dry weight, respectively, our copper concentrations were much lower. The chromium concentration in tadpoles from Watson Lake does fall with the range of tadpole chromium concentrations from the ash basin. However, no malformed frogs were detected in Granite Creek or Watson Lake, unlike those found in the ash basins in South Carolina (Hopkins et al. 2000).

Copper was the most elevated liver metal concentration (30.83 ppm dry weight or 7.70 ppm wet weight) compared to whole body bullfrogs. However, Jenkins (1980) found a *Rana temporaria* liver concentration of 318.9 ppm wet weight downstream of a mercury mine in Yugoslavia. Our bullfrog liver copper concentrations were lower than Jenkins (1980), although his site probably had more available metals to the biotic inhabitants.

Mercury concentrations in tadpoles are similar to those in crayfish. Unlike copper and chromium, adult bullfrogs had a greater mercury concentration (0.38 ppm dry weight) than tadpoles (0.06 ppm dry weight). Adult bullfrogs in Watson Lake contained 0.14 ppm wet

weight mercury. Jenkins (1980) describes background mercury concentrations in *Rana catesbeiana* as 0.1 ppm wet weight and < 0.08 ppm wet weight in *Rana temporaria* in Yugoslavia. Watson Lake adult bullfrogs have similar concentrations of mercury in comparison to ranids in reference areas worldwide.

Selenium and mercury were sequestered in bullfrog livers. Compared to background concentrations, 0.56 ppm wet weight liver selenium is below the range of liver selenium concentrations in Jenkins (1980). Bullfrog selenium concentrations were also well below the suggested 4 ppm national tissue-based selenium criterium. It is very unlikely that adverse effects would occur to bullfrogs as a result of exposure to trace metals in Granite Creek or Watson Lake.

Fish: Arsenic in green sunfish and golden shiners from Granite Creek was 3-times greater than the NCBP 85<sup>th</sup> percentile. A nationwide study of various fish species from 1976 – 1977 found that the range of arsenic in whole fish was 0.05 - 2.9 ppm wet weight (Lima et al. 1984). Although extensive toxicological information is available on the acute effects of arsenic, little is known about the chronic effects in fish at sublethal exposures. Secondary hazards of arsenic poisoning to avian predators are also unknown. Cadmium was only elevated in largemouth bass at Lynx Lake. This sample was only slightly above the 85<sup>th</sup> percentile. Cadmium poisoning to secondary predators might be expected if cadmium in fish exceeded 0.01 ppm wet weight (Eisler 1985) and this was not the case at Lynx Lake. Five out of the seven copper means in different fish species exceeded the NCBP 85<sup>th</sup> percentile, which ranged from 1.2 to 3.6-times higher than the 85th percentile. The no effect level of copper in whole body fish is <9.8 ppm dry weight. From 9.8-13.3 is a "level of concern", and 13.3 ppm copper is considered the toxic threshold (USDOI 1998). Implications for effects to secondary predators are minimal since copper is not a carcinogen or a teratogen. Since none of the fish samples exceeded the no effect level of copper in whole body fish (Appendices 1, 4, 5), we do not expect that fish in Granite Creek and Watson Lake will exhibit any toxicity or abnormalities.

There are no NCBP data to compare the tissue chromium concentrations against. Eisler (1986) is unclear about the significance of chromium residues, but states that residues over 4 ppm dry weight reflect chromium contamination. All of our fish samples were over the 4 ppm dry weight threshold, the greatest being largemouth bass from Lynx Lake (60.51 ppm dry weight). Ecological Analysts (1981) suggests less than 200 ppb wet weight chromium in animal tissues for protection of resources. All of our samples exceeded this criterion also.

Two fish samples, Granite Creek green sunfish and golden shiners, exceeded the NCBP 85<sup>th</sup> percentile for mercury. Our concentrations were greater than the range of background concentrations (<0.05–0.14 ppm wet weight) found by Henderson and Shanks (1973) in the Southwest. Also, the maximum concentration above which mercury effects sensitive fisheating avian predators is about 0.1 ug/g wet weight (Eisler 1987). The means of five of our samples exceeded this criteria: green sunfish and golden shiners in both Granite Creek and

Watson Lake and largemouth bass in Watson Lake. The highest concentration of mercury was in largemouth bass (0.76 ppm dry weight). Because mercury bioaccumulates up the food chain and largemouth bass are probably the primary predatory fish in Watson Lake, it is intuitive that the highest mercury concentration would be in bass. However, mercury in largemouth bass was not statistically different from golden shiner, which had the next highest mercury concentration. Golden shiners are not a predatory fish, so we cannot explain why golden shiners had higher mercury concentrations than bluegill or green sunfish. Mercury was also significantly greater in largemouth bass from Watson Lake than in Lynx Lake. This is an interesting observation for the region because the entire area is highly mineralized. With historical mining present upstream of Lynx Lake and no significant differences among the other metals (Table 6), we cannot account for the greater amount of mercury in Watson Lake bass. Perhaps mercury is greater due to inputs into Granite Creek, such as Southwest Forest Industries, the VA, or the wastewater treatment plant.

None of our samples exceeded the selenium NCBP 85<sup>th</sup> percentile, nor did any of them exceed the 2.0 ppm dry weight threshold for 'normal' food chain selenium accumulation in an aquatic environment (Ohlendorf et al. 1990). The selenium threshold for toxic effects to fish and avian predators is 3 ppm dry weight (Lemly 1993). Little is known about zinc bioaccumulation and its risk to fish and avian predators although 3 zinc samples exceeded the NCBP 85<sup>th</sup> percentile. In summary, high concentrations of arsenic, chromium, and mercury in fish were found in Granite Creek, Watson Lake, and Lynx Lake.

Birds: The gmean wet weights of all red-winged blackbird eggs were within background levels as described in Eisler (As 1988; Cr 1986; Cu 1998; Hg 1987; Se 1985) although none of Eisler's reports had data specifically for red-winged blackbirds' eggs. Also, no arsenic data were available for eggs, so we used whole starling data as a surrogate (Eisler 1988). Arsenic and selenium in the black phoebe egg (0.56 ppm wet weight and 0.46 ppm wet weight, respectively) were greater from Granite Creek than arsenic in the whole starling (< 0.01 - 0.21 ppm wet weight) and selenium in white-faced ibis eggs (0.3 - 1.1 ppm wet weight) and brown pelican eggs (0.19 - 0.38 ppm wet weight) (NAS 1977; King et al. 1980; Blus et al. 1977).

Other individual egg metal concentrations that exceeded levels of concern included 25.4 ppm dry weight boron, 1.19 ppm dry weight mercury, and 3.33 ppm dry weight selenium. The U.S. Department of Interior (USDOI 1998) level of concern for boron in eggs is from 13 - 20 ppm dry weight. The red-winged blackbird egg with an elevated boron level is still below the USDOI lowest observable adverse effect level of > 30 ppm dry weight. The red-winged blackbird egg with 1.19 ppm dry weight mercury is above the background level of < 1 ppm dry weight, but below the toxic threshold of > 4 ppm dry weight (Ohlendorf 1993). The red-winged blackbird egg with 3.33 ppm dry weight selenium is also above the background concentration for selenium in eggs (< 3.0 ppm dry weight), but is below the > 6.0 ppm dry weight toxic threshold (Skorupa 1998).

## *Organochlorine residues*–

Sediment: Total PCB concentrations in sediment were the same, at both Sites 1 and 2, and did not exceed any SQuiRT threshold levels. Trans-nonachlor was detected in Granite Creek sediment at concentrations similar to background concentrations in the literature (<0.1 ppb trans-chlordane; IARC 1979). DDE was detected in the sediment in Granite Creek below threshold effect concentrations (<1.42 ppb dry weight; Buchman 1999).

Crayfish: Total PCBs in crayfish were similar to sediment concentrations. Although there is not a PCB criterion for protection of crayfish, the criterion for protection of fish is < 0.4 ppm wet weight. Our samples were at least 15-times less than this criterion, so crayfish are not at risk from PCB contamination in Granite Creek. Trans-nonachlor is not a threat to crayfish in Granite Creek because it was detected at background concentrations (as compared to trans-chlordane; Eisler 1990, Dowd et al. 1985). Blus (1996) estimated that the lowest dietary concentration of p,p'-DDE that resulted in eggshell thinning and decreased production in the peregrine (*Falco peregrinus*) was 1.0 ppm wet weight. All of our crayfish samples from Granite Creek were at least 300-times below this threshold level. These are the lowest DDE concentrations in crayfish reported for the surrounding area (King et al. 2000; Roberts 1996).

Fish: As previously mentioned, the criterion for fish protection against PCBs is < 0.4 ppm wet weight. None of the fish samples from Granite Creek exceeded this criterion. At most, the Site 2 green sunfish sample was 1/6<sup>th</sup> the recommended criterion. It appears that fish are not at risk from total PCB contamination in Granite Creek. Fish p,p'-DDE concentrations in Granite Creek are lower than the 0.5 ppm level that represents the lower limit of concern for eggshell thinning in bald eagles (USFWS 1986). All fish tissue concentrations were similar to the no observed effect level (NOEL) for chlordane, < 0.01 ppm wet weight (Eisler 1990). There is no risk from organochlorine insecticides or PCBs in sediment, crayfish, or fish to predatory birds in the Granite Creek drainage.

## PAHs and PCP-

Sediment: Forty-two PAHs were analyzed in Granite Creek sediment. In general, Site 1 sediments had greater PAH concentrations than Site 2 sediments (Appendix 1). This is due to Site 1 sampling location's proximity to Slaughterhouse Gulch, the tributary of Granite Creek that runs adjacent to the Superfund site. Threshold effects levels (TELs) in NOAA SQuiRTs range from 31.7 ppb dry weight benzo(a) pyrene to 111 ppb dry weight fluoranthene. Threshold effects levels are similar to no observable effect levels (NOELs) in that they demarcate the concentration in sediment at which organisms begin to exhibit decreased growth or survival. Our sediment PAH concentrations were higher than the TELs but lower than the probable effects level, which ranged from 385 - 2355 ppb dry weight (Buchman 1999). Pentachlorophenol was greater in Site 1 sediment than in Site 2 sediment. This correlates with Site 1's proximity to the Superfund Site and Site 2's distance (1.14 mi (1.83 km) down Granite Creek) from the Site 1. Due to a lack of good reference data and

threshold levels for pentachloro-anisole, only within sample comparisons were possible. Pentachlorophenol was lower in Granite Creek when compared to a background concentration in Bay of Quinte, Lake Ontario (60 ppb dry weight; Fox and Joshi 1984).

Crayfish: Polycyclic aromatic hydrocarbons were detected in a few crayfish. Of those PAHs that were detected, acenaphthene had the highest concentration, but benzo(a)pyrene, phenanthrene, pyrene, and fluoranthene were also detected. Polycyclic aromatic hydrocarbon concentrations found in crayfish were lower than those in sediment. Pentachlorophenol was not detected in crayfish; pentachloro-anisole was detected at Site 1, but not at Site 2. Polycyclic aromatic hydrocarbons do not appear to be a problem in crayfish in Granite Creek as a result of Southwest Forest Industries' activity.

Fish: In general, fish PAH and PCP concentrations were lower than the reported sediment concentrations. This is due to rapid PAH metabolism by fish (Lawrence and Weber 1984). Eisler (1987) provides no recommended level for protection of sensitive fish, but does note that whole body residues greater than 300 ppb benzo(a)pyrene in certain teleosts induces detoxifying enzymes. None of the fish in Granite Cræk have PAH residues anywhere near 300 ppb. Only one fish sample, green sunfish collected at Site 2, had a detectable pentachlorophenol concentration (32.2 ppb wet weight). This is the opposite of the PCP trend in the sediment, with greater upstream concentrations than downstream. Since fish are mobile, it may be that the green sunfish composite sample contained one fish that had been in Slaughterhouse Gulch while it was flowing. Or, since sediments are heterogenous, perhaps there is a pocket of elevated PCP sediment to which these downstream fish were exposed. Fish pentachloro-anisole trends were as expected: upstream fish had higher concentrations than downstream fish. Pentachlorophenol and other wood treatment-related products have been deposited into Granite Creek. Levels of PAHs and PCP are higher than background and threshold effect levels, but are still low enough not to elicit acute toxicity either to the fish in the ambient environment or to secondary predators. Although there is no residue threshold for PCP, Eisler (1989) recommended the use of human guidelines for wildlife in the interim. As such, the human NOEL for food was 30 ppb (USEPA 1980). Pentachlorophenol in Site 2 green sunfish was 32.2 ppb wet weight. Since the Granite Creek sample was close to the human NOEL, we do not suspect any secondary poisoning potential in the fish in Granite Creek. We can also compare this concentration against mean concentrations nationwide (Irwin et al. 1997): 0.002 ppm in Lake Michigan to 16.38 ppm in the Pacific Northwest. The green sunfish PCP concentration is well within this range.

## Dioxins and furans-

Sediment: Our sediment TCDD concentrations were below the SQuiRT Upper Effects Threshold and below the EPA's sediment guidance level. Therefore, we expect no adverse effects due to dioxins and furans in the sediment to the biota in Granite Creek.

Crayfish: The 2,3,7,8-TCDD made up a very small fraction of the total amount of total dioxin and furan concentration. Because TCDD was not abundant in crayfish samples, the total dioxin plus furan concentration was much greater than the crayfish TEQ (Figure 2). The crayfish TEQ was smaller than the sediment TEQ, but greater than both fishes TEQs. There is no documented threshold for adverse effects for crayfish, but the crayfish TEQ was below the EPA's 50 ppt threshold for low risk to a predatory fish. In summary, predators are not at risk for dioxin or furan poisoning after consuming crayfish in Granite Creek because crayfish dioxin and furan concentrations are lower than threshold levels for fishes.

Fish: Only three dioxins and furans were detected in fish samples. TEQs were higher in golden shiners than in green sunfish. Both fish TEQs were lower than the sediment and crayfish TEQs. Since Granite Creek and Watson Lake whole body fish TEQs are below EPA's 50 ppt threshold, there is no risk at this site to predatory fishes due to the Southwest Forest Industries Superfund Site.

#### **CONCLUSION**

It appears that the former Southwest Forest Industries, current Superfund Site, has had minimal effect upon the Granite Creek/Watson Lake watershed. Levels of arsenic, chromium, and copper were detected in biota above threshold concentrations. Fish were contaminated with arsenic and chromium, yet the consequences of elevated arsenic and chromium tissue concentrations are unknown. Copper concentrations were low enough not to be of ecological significance. Fish tissue PCP concentrations were lower than expected. Pentachlorophenol breaks down rapidly in aquatic environments, with continuous sunlight exposure (Wong and Crosby 1978). It is likely that when the PCP treatment pond was removed from the Southwest Forest Industries site, any biological effects that were occurring ceased (Niimi and Cho 1983). It could also be possible that we did not sample the correct pathways for PCP. What was surprising were the elevated levels of mercury in the fish tissue from Granite Creek and Watson Lake. This mercury could be indigenous to the system or could be anthropogenic in nature.

However, at our comparison site, Lynx Lake, we found elevated concentrations of cadmium and chromium in fish tissue. Further investigation of these elevated tissue concentrations is warranted.

## RECOMMENDATIONS

We recommend that trace element, especially mercury, monitoring continue in the fishes of Granite Creek and Watson Lake. It is important to sample a wide variety of fishes and locations in order to track trends over time. Mercury could be deposited into this system aerially, naturally through bedrock weathering, or from anthropogenic releases and

amplification in the wastewater treatment plant. Future studies should include the same sampling locations used in this study as well as one below the wastewater treatment plant, one directly below the VA, one site in downtown Prescott, and one site upstream of all of these locations. Monitoring could be spaced out once every 10 years with assistance from Arizona Game and Fish Department. It is important to continue monitoring the Granite Creek and Watson Lake because it is a migratory bird stopover in the arid southwest and it supports many recreational opportunities in the Prescott area.

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Appendix 1. Polyaro matic hydrocarb ons and pentach lorophen of (ppb wet weight) in sediment, crayfish, and fish collected from two locations in Granite Creek, Arizona, 2000-2001.

ocations in Granite Creek, Arizona		liment²	Cra	nyfish³	Green	sunfish³	Golde	n shiner <sup>3</sup>
Compound <sup>1</sup>	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
1-methylnapththalene	<1.25	<1.24	ND <sup>4</sup>	ND	ND	7.46	4.31	ND
1-methylphenanthrene	8.87	7.22	ND	ND	ND	ND	ND	ND
2-methylnaphthalene	1.51	1.50	ND	ND	ND	6.97	ND	ND
Benzo (a) anthracene	117.	92.2	ND	ND	ND	ND	ND	ND
C1-fluoranth enes & pyrenes	46.6	29.5	ND	ND	ND	ND	ND	ND
C1-phenan threnes & anth racenes	26.0	20.0	ND	ND	13.4	ND	2.63	ND
C1-chrysenes	40.2	34.5	ND	ND	ND	ND	ND	ND
C1-dibenzothiophenes	1.49	1.24	ND	ND	ND	ND	ND	ND
C1-fluorenes	4.10	2.94	3.94	ND	10.1	2.65	39.9	13.8
C1-naphthalenes	2.67	2.39	ND	ND	2.96	14.4	6.06	ND
C2-phenan threnes & anthracenes	7.48	8.18	ND	ND	ND	ND	ND	ND
C2-chrysenes	8.53	10.2	ND	ND	ND	ND	ND	ND
C2-fluorenes	3.23	1.80	3.7	ND	2.54	ND	2.61	ND
C2-napht halenes	1.72	1.92	ND	ND	3.90	ND	10.2	ND
C3-phenth renes & anthrac enes	2.83	3.49	ND	ND	ND	ND	ND	ND
C3-chrysenes	1.29	2.08	ND	ND	ND	ND	ND	ND
C3-fluorenes	<1.25	<1.24	6.74	ND	ND	ND	ND	ND
C3-napht halenes	1.44	<1.24	ND	ND	4.16	ND	7.2	ND
C4-phenan threnes & anthracenes	<1.25	1.40	ND	ND	ND	ND	ND	ND
C4-chrysenes	4.34	4.09	ND	ND	ND	ND	ND	ND
Acenaphthalene	3.03	3.29	ND	ND	ND	ND	3.24	ND
Acenaphthene	14.0	7.58	20.9	ND	32.1	ND	80.1	ND
Anthracene	4.07	3.82	ND	ND	3.06	3.02	8.17	ND
Benzo (a) pyrene	222.	151.	4.34	ND	ND	ND	3.17	ND
Benzo (b) fluoranthene	173.	121.	4.10	ND	ND	4.96	ND	ND
Benzo (e) pyrene	102.	66.0	3.04	ND	ND	ND	ND	ND
Benzo (g,h,i) perylene	128.	84.0	3.16	ND	ND	ND	2.86	ND
Benzo (k) fluoranthene	48.3	36.8	ND	ND	ND	ND	2.46	ND
Biphen yl	ND	ND	ND	ND	3.22	5.37	7.56	ND
Chrysene	162	103	4.51	ND	ND	5.18	2.70	ND
Dibenzo (a,h) anthracene	26.2	17.5	ND	ND	ND	ND	ND	ND
Dibenzothiophene	5.53	3.48	ND	ND	ND	ND	ND	ND
Fluoranthene	281	182	8.00	4.23	3.62	14.7	3.76	ND
Fluorene	18.30	10.60	11.7	ND	31.4	ND	75.0	ND
Indeno (1,2,3-c,d) pyrene	141	90.3	2.97	ND	ND	ND	ND	ND
Naphthalene	4.33	4.53	ND	ND	ND	16.50	3.11	ND
Perylene	27.0	21.5	ND	ND	ND	ND	ND	ND
Phenanthrene	176	114	4.82	2.48	2.81	6.35	2.65	ND
Pyrene	260.	172	6.94	3.72	ND	4.2	4.06	ND
Pentachlorophenol	21.2	5.44	ND <sup>5</sup>	ND	ND	32.2	ND	ND
Pentachloro-anisole	0.18	$ND^6$	0.50	ND	2.26	1.23	3.42	2.02

<sup>1</sup>1,6,7-trimethyl-naphthalene, 2,6-dimethylnaphthalene and C2-dibenzothiophenes were not detected in any samples. <sup>2</sup>One sediment sample was collected per site. <sup>3</sup>Two composite samples were collected at each location: data points represent an average except where one sample was a non-detect and the other had a reported value. In this case, the reported value is shown in italics. <sup>4</sup>Detection limits ranged from 2.43 to 2.47 ppb for PAHs. If no PAHs were detected in the sample, then ND (not detected) is listed in the column. <sup>5</sup>PCP detection limits ranged from 9.72-9.86 ppb. <sup>6</sup>Pentachloro-anisole detection limits ranged from 0.12 to 0.25 ppb.

Appendix 2. Metals in sediment, crayfish, fish, and bullfrog tadpoles from Granite Creek Arizona, 2000.

						Contamin	nant conc	entration	n, ppm	dry weigh	ıt <sup>ı</sup>									Moist
Species	Site <sup>2</sup>	Al	As	В	Ba	Be	Cd	Cr	Cu	Fe	Hg³	Mg	Mn	Ni	Pb	Se	Sr	V	Zn	(%)
Sediment	1	8670	13.0	< 2.00	105	0.48	< 0.20	33.8	18.7	15572	< 0.20	6956	1009	43.4	11.8	<1.00	68.9	28.6	50.6	23.1
Sediment	2	6402	5.37	< 2.00	73.4	0.38	< 0.20	21.4	12.4	9997	< 0.20	3903	218	26.6	11.3	<1.00	39.0	20.1	31.4	29.5
Crayfish	1	630	3.06	< 2.00	279	< 0.10	0.19	16.5	64.0	699	< 0.20	2907	622	2.63	1.90	< 0.50	622	4.85	39.8	75.3
Crayfish	1	311	2.91	< 2.00	289	< 0.10	< 0.10	16.3	47.2	496	0.22	2385	1236	2.29	2.10	< 0.50	675	4.85	39.0	75.3
Crayfish	2	450	4.42	2.04	302	< 0.10	0.19	15.7	32.3	1250	< 0.20	3137	1430	4.93	2.20	< 0.50	758	5.60	41.9	75.0
Crayfish	1	481	1.47	<2.00	146	< 0.10	< 0.10	14.7	43.1	575	< 0.20	2044	347	1.59	1.27	< 0.50	531	3.46	44.1	75.6
Green sunfish	1	89.2	0.79	<2.00	12.9	< 0.10	< 0.10	10.2	3.24	152	0.46	1884	66.2	0.73	< 0.50	< 0.50	118	2.17	149	77.0
Green sunfish	1	43.2	0.63	<2.00	9.54	< 0.10	< 0.10	8.91	4.61	107	0.73	1462	31.2	< 0.50	< 0.50	< 0.50	119	2.31	90.7	78.0
Green sunfish	2	203	1.10	<2.00	11.4	< 0.10	< 0.10	8.85	3.32	309	0.32	1693	72.2	0.71	< 0.50	< 0.50	91.8	2.34	112	76.5
Green sunfish	2	169	0.59	<2.00	5.89	< 0.10	< 0.10	7.52	3.23	243	0.31	1311	37.3	0.66	< 0.50	< 0.50	53.6	1.95	83.1	79.8
Golden shiner	1	168	0.87	<2.00	21.7	< 0.10	< 0.10	8.15	2.89	261	0.62	1553	60.4	0.72	< 0.50	< 0.50	101	1.73	177	74.7
Golden shiner	1	485	0.89	<2.00	19.2	< 0.10	< 0.10	12.0	3.83	664	0.90	2107	73.2	1.66	0.90	< 0.50	163	3.09	270	80.6
Golden shiner	2	372	0.74	<2.00	16.9	< 0.10	< 0.10	11.0	3.51	515	0.92	2015	64.0	1.30	< 0.50	< 0.50	163	2.28	194	77.9
Golden shiner	2	85.4	0.66	<2.00	9.12	< 0.10	< 0.10	8.01	3.18	158	0.70	1490	21.4	< 0.50	< 0.50	< 0.50	92.9	1.44	189	76.0
B frog tadpole	2	5645	4.82	2.18	59.3	0.24	0.11	17.0	15.6	6161	< 0.20	2477	338	12.7	6.71	0.57	134	10.6	72.8	85.1
Detection Limit		2.5	0.5	2.0	1.0	0.1	0.1	0.5	0.5	5.0	0.05	5.0	0.5	0.5	0.5	0.5	0.5	0.5	1.0	

<sup>1</sup>Molybdenum was not detected in any samples. <sup>2</sup>Site: Site 1 = First 50 m below industrial park bridge. Site 2= Adjacent to, and slightly downstream from, Riparian Area parking lot. As, Cu, Hg, and Zn in all fish samples exceeded the NCBP 85<sup>th</sup> percentile. <sup>3</sup>0.30 ppm dry weight (dw) = approximately 0.06 ppm wet weight (ww). 0.90 ppm dw = approximately 0.20 ppm ww. Food chain: 3 ppm Hg (dry weight) in earthworms should be considered hazardous to sensitive species that eat earthworms. (Beyer and Stafford 1993). For the protection of sensitive species of mammals and birds that regularly consume fish and other aquatic organisms, total mercury concentrations in these prey items should probably not exceed 0.1 ppm fresh weight for birds, and 1.1 ppm for small mammals (Eisler 1987). The maximum concentration above which effects on fish-eating avian predators can be expected is 0.1 ppm wet weight (Eisler 1987). For mammals eating fish the concern level is 1.1 ppm wet weight (Eisler 1987). To protect fish and predatory organisms, total mercury burdens in these organisms should not exceed 0.5 ppm wet weight (Walsh et al. 1977). For piscivorous birds, dietary concentrations of methyl mercury that produce overt neurological effects in adult birds are five times greater than dietary concentrations that cause significant reproductive impairment (Scheuhammer 1991, Scheuhammer 1987). Mercury concentrations of 0.3 to 0.4 ppm wet weight in prey of common loons were sufficient to impair territorial fidelity and egg laying (Barr 1986).

Appendix 3. Metals in crayfish collected from Watson Lake, Arizona, 2000.

				]	Metal co	oncent	ration,	ppm o	dry wei	ght¹						Moist
Al	As	В	Ba	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Ni	Se	Sr	V	Zn	(%)
592.	0.60	<2.08	241.	0.36	0.75	25.6	557.	0.05	3744.	134.	1.97	1.05	691.	0.64	63.0	71.0
275.	1.09	3.40	208.	0.28	15.3	51.1	369.	0.18	4700.	290.	4.84	1.81	968.	< 0.49	74.8	50.3
621.	< 0.54	2.38	196.	0.31	0.69	43.2	526.	0.11	3778.	147.	1.58	1.54	636.	0.70	58.8	65.5
265.	< 0.51	< 2.06	225.	0.13	< 0.51	38.5	272.	0.08	3491.	156.	< 0.51	1.64	735.	< 0.51	71.8	65.0
114.	1.80	2.52	246.	< 0.11	18.5	36.2	207.	0.10	3437.	102.	5.92	2.21	741.	< 0.54	67.1	63.1
301.	< 0.50	<1.99	241.	0.11	< 0.50	41.9	286.	0.11	4137.	192.	0.90	2.26	684.	< 0.50	74.4	64.7
487.	0.73	<2.03	134.	0.20	< 0.51	52.1	306.	0.08	2985.	97.3	0.73	1.74	651.	< 0.51	71.0	68.2
234.	< 0.48	<1.92	223.	0.18	22.5	36.4	400.	0.10	3090.	148.	9.90	1.71	595.	< 0.48	76.5	66.0
218.	< 0.47	<1.86	144.	0.12	7.14	33.5	362.	0.13	2590.	99.8	3.65	1.12	391.	< 0.47	72.6	67.3

<sup>&</sup>lt;sup>1</sup>Beryllium, molybdenum, lead, and vanadium were not detected in any samples.

Appendix 4. Metals in bullfrog tadpoles and in bullfrog whole body and liver tissues collected from Watson Lake, Arizona, 2001.<sup>1</sup>

zako, m	Concentration ppm dry weight <sup>2</sup>																	
Sample																		Moist
	Al	As	В	Ba (	Cd (	Cr Cı	ı Fe	Hg	Mg	Mn	Ni I	Pb S	e Si	r V	Zn			(%)
Tadp2	4455.	<0.50	<1.99	78.2	1.24	8.48	7.11	3550.	0.06	2530.	88.6	12.3	$ _{< 0.50}$	<0.50	55.2	7.02	47.6	76.7
Tadp3	3497.	<0.50	<1.98	72.6	1.12	6.94	8.17	2830.	0.06	2166.	67.6	10.2	<0.50	<0.50	57.8	5.70	44.3	73.9
Tadp3	4907.	<0.50	<2.00	92.0	1.34	8.41	8.89	3810.	0.06	2641.	144.	12.2	2.25	<0.50	60.7	7.32	50.5	75.1
Tadp5	5988.	2.08	2.23	93.9	1.96	18.1	9.72	5751.	0.05	2854.	605.	15.4	1.10	< 0.50	62.9	9.72	46.1	73.9
Tadp6	2701.	< 0.50	<1.99	65.8	1.03	5.71	8.69	2310.	0.05	1915.	128.	7.58	0.95	< 0.50	46.7	4.60	54.9	75.7
Tadp7	4338.	0.83	<1.99	66.3	1.65	8.96	9.13	4394.	0.07	2328.	323.	8.56	0.91	< 0.50	40.8	7.06	55.5	75.7
Tadp8°	6317.	< 0.50	3.85	97.5	0.61	84.2	11.6	5062.	0.10	3314.	232.	29.2	0.63	1.26	85.3	10.2	54.3	76.3
Tadp9	5267.	< 0.50	<2.00	94.1	1.48	31.9	7.70	4322.	0.05	2782.	127.	19.3	< 0.50	< 0.50	62.5	7.85	45.3	75.2
Tadp10	3885.	0.53	<1.99	76.9	1.33	52.0	7.03	3557.	< 0.05	2153.	163.	16.6	< 0.50	< 0.50	46.2	5.90	43.2	72.0
Tadp11 <sup>3</sup>	6024.	1.07	3.92	96.4	1.90	56.6	20.4	5589.	0.08	3031.	169.	44.6	1.22	< 0.50	72.1	8.88	538.	81.4
Tadp12	5048.	< 0.50	<2.01	69.8	1.32	35.9	8.44	3720.	0.11	2639.	81.9	15.5	< 0.50	< 0.50	56.4	7.02	53.8	84.1
WB1	60.5	0.95	< 2.00	28.9	< 0.10	64.6	5.07	476.	0.57	2083.	23.1	16.3	< 0.50	1.18	90.8	< 0.50	109.	60.1
WB2	275	1.33	<2.00	18.8	< 0.10	46.4	3.98	250.	0.64	2365.	18.7	9.04	< 0.50	1.88	110.	< 0.50	100.	63.0
WB3	27.3	< 0.50	<1.99	14.0	< 0.10	0.54	1.93	55.2	0.46	1506.	12.2	< 0.50	< 0.50	< 0.50	59.3	< 0.50	77.5	63.7
WB5	211	0.91	< 2.00	21.6	< 0.10	38.2	2.73	406.	0.46	2251.	21.7	7.76	< 0.50	0.78	111.	< 0.50	96.6	65.0
WB6	10.3	2.21	<1.99	31.2	< 0.10	13.2	2.22	121.	0.23	2169.	19.8	1.74	< 0.50	1.51	112.	< 0.50	113.	62.0
WB7	88.3	0.90	< 2.00	26.9	< 0.10	16.4	3.08	202.	0.18	2217.	26.4	2.92	< 0.50	1.30	106.	< 0.50	95.5	67.0
WB8	59.8	2.28	2.34	33.9	< 0.10	4.53	1.69	103.	0.50	1718.	16.9	1.02	< 0.50	2.30	91.2	< 0.50	92.0	64.3
WB9	88.6	0.61	2.17	21.6	< 0.10	7.31	2.52	139.	0.15	2067.	16.1	0.95	< 0.50	1.66	73.9	< 0.50	92.0	61.0
WB10	17.9	20.7	< 2.00	22.1	< 0.10	49.6	3.17	315.	0.62	2346.	26.6	10.3	< 0.50	1.07	93.6	< 0.50	108.	63.1
Liver1	56.9	0.96	<1.99	6.74	0.50	< 0.50	67.6	1128.	2.38	707.	7.27	< 0.50	< 0.50	2.91	2.28	1.37	69.4	75.8
Liver2	5.39	< 0.50	< 2.00	2.68	0.33	< 0.50	4.76	848.	1.29	577.	5.59	< 0.50	< 0.50	2.00	0.69	< 0.50	50.8	72.0
Liver3	< 2.50	< 0.50	< 2.00	<1.00	0.18	< 0.50	13.2	211.	0.51	312.	2.67	< 0.50	< 0.50	0.54	1.03	< 0.50	38.8	70.9
Liver4	5.06	< 0.50	<1.99	2.14	0.19	< 0.50	13.4	497.	0.65	377.	3.66	< 0.50	< 0.50	1.14	0.53	< 0.50	48.4	72.7
Liver5	24.6	< 0.50	< 2.00	1.83	0.18	< 0.50	7.98	422.	1.01	442.	3.40	< 0.50	< 0.50	1.77	0.93	< 0.50	58.5	74.4
Liver6	6.70	0.54	<2.00	5.61	0.75	< 0.50	31.6	479.	0.45	440.	4.09	< 0.50	< 0.50	1.07	< 0.50	0.59	56.2	73.5
Liver7	48.8	< 0.50	<2.00	3.85	0.15	< 0.50	113.	451.	0.40	537.	24.9	< 0.50	< 0.50	1.64	3.05	0.56	74.5	75.9
Liver8	9.58	< 0.50	<1.98	7.69	1.07	< 0.50	109.	1717.	1.17	494.	6.59	< 0.50	< 0.50	2.97	1.30	2.73	72.7	81.1
Liver9	10.9	0.71	<1.96	3.50	0.45	0.49	164.	466.	0.29	605.	17.1	0.76	< 0.49	2.37	1.02	0.78	89.5	76.1
Liver10	42.4	< 0.46	<1.84	8.30	0.60	0.48	26.8	467.	0.13	605.	6.80	< 0.46	< 0.46	5.22	1.64	1.36	85.1	76.3

<sup>&</sup>lt;sup>1</sup>Whole body sample minus liver and gastrointestinal tract.

<sup>&</sup>lt;sup>2</sup>Beryllium was not detected in any samples.

<sup>&</sup>lt;sup>3</sup>Molybdenum was present in 2 tadpole samples at 1.34 and 1.32 ppm.

Appendix 5. Metals in bluegill sunfish, green sunfish, and golden shiner collected from Watson Lake, Arizona, 2000.

Lake, Aliz					Cor	ncentra	tion, p	pm dry	weight	1				Moist
Sample	Al	As	Ba	Cr	Cu	Fe	Hg	Mg	Mn	Ni	Se	Sr	Zn	(%)
Bluegill	159.	< 0.05	14.8	27.0	2.20	286	0.21	1747	70.2	5.53	0.58	126.	101.	73.2
Bluegill	106.	< 0.05	14.1	25.7	2.24	251	0.27	1725	70.2	4.96	< 0.50	105.	112.	72.2
Bluegill <sup>2</sup>	167.	0.73	12.1	99.5	5.23	719	0.25	1829	99.8	22.1	< 0.50	97.0	98.4	70.0
Bluegill	120.	0.53	9.90	27.5	2.99	255	0.23	1672	48.2	5.74	0.56	101.	89.8	72.7
Bluegill	96.4	< 0.05	12.9	33.3	2.59	271	0.23	2042	52.2	6.79	0.58	136.	103.	73.0
Bluegill	334.	1.89	14.8	20.7	2.63	370	0.26	2171	127.	5.13	1.44	112.	123.	78.5
Bluegill	98.1	< 0.05	8.43	30.5	2.54	247	0.23	1988	36.9	6.90	1.06	107.	102.	70.0
Bluegill	103.	< 0.05	11.7	14.2	1.85	157	0.27	1952	36.6	2.90	1.24	107.	98.1	71.2
Bluegill	122.	< 0.05	15.8	23.3	2.10	198	0.21	1768	51.1	4.11	< 0.50	101.	88.6	71.2
Bluegill	104.	< 0.05	8.83	37.4	2.56	331	0.22	1906	58.7	6.54	1.27	86.7	97.4	68.0
Green S.3	167.	< 0.05	13.3	1.02	1.51	88.0	0.23	2514	64.4	< 0.50	0.91	131.	132.	76.1
Green S.	165.	< 0.05	11.6	0.79	1.62	70.3	0.20	2211	51.1	< 0.50	1.63	120.	116.	75.2
Green S.4	200.	< 0.05	18.1	0.97	1.56	109.	0.21	2539	123.	< 0.50	1.06	122.	120.	76.3
Green S.	450.	0.51	9.30	0.74	1.61	67.7	0.35	2093	30.8	< 0.50	0.67	98.4	144.	73.1
Green S.	447.	0.85	14.9	1.47	1.60	310.	0.20	2424	77.8	< 0.50	1.01	115.	110.	75.7
Green S.	48.1	< 0.05	4.21	3.38	1.48	96.0	1.26	1875	14.2	< 0.50	1.05	92.3	110.	72.0
Green S.	75.6	0.65	6.57	8.25	3.69	153.	0.69	1939	11.8	1.24	1.68	111.	95.4	74.0
Green S.	162.	< 0.05	9.38	10.4	1.68	181.	0.47	2203	41.6	1.94	0.84	128.	95.1	76.1
Green S.	48.5	1.70	9.42	16.1	2.10	324.	0.66	2133	40.0	17.0	163.	< 0.50	111.	76.0
Green S.5	395.	1.10	13.3	53.4	3.29	441.	0.24	2265	63.5	12.1	0.80	131.	130.	74.1
Golden S.	171.	< 0.05	12.0	75.7	5.11	595.	0.56	2090	17.1	15.7	1.03	116.	250.	73.2
Golden S.	137.	< 0.05	12.2	70.1	5.12	530.	0.62	2143	14.0	15.0	1.13	129.	197.	73.5
Golden S.6	51.9	0.66	13.7	125.	7.54	863.	0.70	2087	20.0	28.2	0.57	127.	203.	73.5
Golden S.	303.	1.17	16.8	58.4	3.97	528.	0.76	2443	22.5	13.6	2.16	212.	265.	74.2
Golden S.	90.7	1.53	13.9	32.2	3.33	275.	0.70	2129	14.5	7.36	1.59	160.	261.	75.0
Golden S.	350.	0.54	21.6	25.5	3.82	272.	0.52	2034	14.8	7.20	1.08	128.	211.	73.4
Golden S.	105.	0.62	11.4	62.8	4.33	478.	0.51	18.37	16.0	16.1	0.84	104.	164.	70.1
Golden S.	140.	0.86	14.5	57.2	4.82	474.	0.56	2221	17.0	14.7	1.60	139.	213.	72.2
Golden S.	98.9	0.57	16.3	43.5	3.99	357.	0.46	1770	14.5	10.4	1.13	107.	183.	69.5
Golden S.	161.	0.93	19.3	59.7	5.53	524.	0.65	2203	23.5	15.1	1.05	144.	184.	72.2

<sup>&</sup>lt;sup>1</sup>Berllium and lead were not detected in any samples.

<sup>&</sup>lt;sup>2</sup>One bluegill sunfish sample also contained 1.39 ppm molybdenum and 0.63 ppm vanadium.

<sup>&</sup>lt;sup>3</sup>This sample contained 2.05 ppm boron.

<sup>&</sup>lt;sup>4</sup>Cadmium was present at 0.22 ppm.

<sup>&</sup>lt;sup>5</sup>Vanadium was detected in one green sunfish at 0.64 ppm.

<sup>&</sup>lt;sup>6</sup>Molybdenum was recovered in one golden shiner at 1.77 ppm.

Appendix 6. Metals in largemouth bass collected from Watson and Lynx Lakes, Arizona, 2001.

		Concentration, ppm dry weight <sup>1</sup>														Moist
Sample	Area	 A1	As	Ва	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Ni	Se	Sr	Zn	(%)
LMB	Watson	9.97	< 0.50	3.43	< 0.10	57.8	4.56	462	0.57	1885	9.90	13.5	1.38	123.	54.0	58.2
LMB	Watson	17.0	< 0.50	2.34	< 0.10	6.99	1.61	82.0	1.23	1987	5.26	0.69	1.16	99.1	69.9	41.5
LMB	Watson	17.7	0.86	3.78	< 0.10	12.6	1.92	115.	0.73	2508	10.1	2.16	1.40	130.	60.9	61.6
LMB	Watson	9.69	< 0.50	2.30	< 0.10	53.6	4.29	421.	0.78	1936	10.8	13.7	1.15	101.	67.1	66.1
LMB	Watson	9.91	0.51	4.12	< 0.10	49.2	3.70	389.	0.82	2408	10.7	11.4	1.45	134.	54.7	67.0
LMB	Watson	11.1	< 0.50	3.07	< 0.10	25.2	2.68	213.	0.61	1775	9.86	5.61	1.30	82.2	62.0	67.3
LMB	Lynx	15.4	< 0.50	4.78	0.22	84.2	3.06	718.	0.27	1505	16.3	6.61	0.94	58.3	51.6	64.7
LMB	Lynx	11.7	< 0.50	3.62	< 0.10	0.71	0.98	56.1	0.28	1411	10.7	< 0.50	1.09	68.8	53.8	39.4
LMB	Lynx	15.4	< 0.50	8.61	0.27	62.0	6.95	433.	0.16	1628	16.5	14.2	0.89	57.3	44.5	43.0
$LMB^2$	Lynx	21.1	< 0.50	5.14	0.16	84.3	4.12	573.	0.14	1763	12.4	13.9	0.93	60.0	61.5	66.3
LMB <sup>3</sup>	Lynx	22.1	0.85	4.53	0.20	123.	2.73	779.	0.15	1892	16.8	3.57	1.86	71.5	160.	69.6

<sup>&</sup>lt;sup>1</sup>Boron, beryllium, lead, and vanadium were not detected in any samples. <sup>2</sup>This sample contained 1.40 ppm molybdenum. <sup>3</sup>This bass sample also contained 1.57 ppm molybdenum.

Appendix 7. Metals in red-winged blackbird, American coot, and black phoebe eggs collected from Granite Creek and Watson Lake, Arizona, 2000-2001.

	Metal concentration, ppm dry weight <sup>1</sup>														Moist
Species <sup>2</sup>	Al	As	В	Ва	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Se	Sr	Zn	(%)
RWBB	6.07	< 0.47	25.4	4.33	< 0.09	< 0.09	1.48	135.	0.51	370.	3.68	3.33	13.2	70.6	84.5
RWBB	5.69	< 0.48	7.87	3.91	< 0.10	< 0.10	2.72	127.	0.61	386.	4.40	1.83	6.93	59.8	83.0
RWBB	4.26	< 0.46	3.53	2.10	< 0.09	0.17	2.45	122.	1.19	307.	3.42	1.39	7.79	54.7	82.0
RWBB	5.63	1.72	2.32	5.58	< 0.09	< 0.46	2.78	146.	0.38	506.	7.27	1.88	10.5	58.7	80.9
RWBB	7.05	< 0.48	2.22	4.76	< 0.10	< 0.48	3.76	126.	0.41	351.	5.54	1.10	7.81	48.7	83.0
RWBB	5.68	0.58	2.14	3.99	0.225	< 0.49	3.00	152.	0.31	404.	3.10	0.95	11.9	55.8	82.1
RWBB	3.10	< 0.50	<1.99	2.74	< 0.10	< 0.50	2.62	152.	0.40	382.	9.97	1.35	4.74	58.4	80.0
RWBB	5.34	< 0.49	<1.95	3.06	< 0.10	< 0.49	2.46	102.	0.40	369.	5.19	1.02	10.1	47.0	77.0
RWBB	5.04	3.16	<1.81	7.47	0.13	< 0.45	3.77	185.	0.44	663.	9.70	2.38	16.7	66.1	81.9
RWBB	4.55	0.58	<2.00	2.98	< 0.10	< 0.50	1.96	151.	0.29	289.	4.66	0.95	6.76	67.9	74.3
RWBB	4.28	< 0.44	<1.78	3.58	0.12	< 0.44	2.51	165.	0.45	346.	4.89	0.95	6.05	58.1	82.0
A. coot	6.37	0.90	0.75	11.5	0.11	0.14	3.02	113.	0.43	382.	3.61	< 0.47	7.02	52.6	73.3
Bl. Phoebe <sup>3</sup>	10.8	3.10	<2.11	8.57	< 0.11	< 0.53	3.61	155.	0.25	825.	2.34	2.55	50.9	77.0	81.9

<sup>&</sup>lt;sup>1</sup>Beryllium, molybdenum, nickel, lead and vanadium were not detected in any samples.

<sup>&</sup>lt;sup>2</sup>Species: Bl. phoebe = black phoebe, A. Coot = American coot, RWBB = red-winged blackbird.

Appendix 8. Organochlorine insecticides and total polychlorinated biphenyls in sediment, crayfish, fish, and tadpoles collected from Granite Creek, Arizona, 2000.

	Concentration, parts per million, wet weight <sup>1</sup>												
Sample	Area coll.	$N^2$	p,p'- DDE	trans- nonachlor	Total PCB	Moist (%)	Lipid (%)						
Sediment	up	1	< 0.01	< 0.01	0.01	23.1	NA						
Sediment	dn	1	< 0.01	< 0.01	0.01	29.5	NA						
Crayfish	up	7	< 0.01	< 0.01	0.03	78.0	1.60						
Crayfish	up	8	< 0.01	< 0.01	0.02	79.4	2.40						
Crayfish	dn	4	< 0.01	< 0.01	0.02	74.8	1.40						
Crayfish	dn	2	< 0.01	< 0.01	< 0.01	76.4	0.50						
Green sunfish	up	18	0.01	0.01	0.08	77.5	1.60						
Green sunfish	up	10	0.01	0.01	0.05	74.4	2.90						
Green sunfish	dn	11	0.01	0.02	0.06	75.0	3.90						
Green sunfish	dn	15	0.01	0.02	0.07	78.3	4.20						
Golden shiner	up	13	0.02	0.01	0.07	73.5	3.10						
Golden shiner	up	10	0.01	< 0.01	0.03	80.6	0.80						
Golden shiner	dn	10	0.01	< 0.01	0.04	77.6	1.20						
Golden shiner	dn	12	0.01	0.01	0.04	72.6	2.60						
Bullfrog tadpole	dn	6	< 0.01	0.01	0.06	85.6	2.60						

<sup>&</sup>lt;sup>1</sup>No other organochlorine compounds were detected.

 $<sup>^{2}</sup>N =$  number of individuals in each composite sample.

Appendix 9. Polyaromatic hydrocarbons in sediment, crayfish, bullfrog tadpoles, and fish collected from two locations in Granite Creek, Arizona, 2000.

rippendix 5. Tory drondere fry dr	ocaroons i	ir seamner	it, crayiis				location collected and contaminant concentration, ppb wet weight									
	Sedi	ment²		Cray	fish³			Green	sunfish4			Golden	shiner		Tadpole	
	06/14/00	06/14/00	04/2	28/00	06/1	4/00	04/2	8/00	06/	14/00	04/2	8/00	06/14/00		06/14/00	
Compound	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 2	
1-methylmapththalene	<1.25	<1.24	<2.44	<2.44	<2.38	< 2.47	< 2.43	7.46	<2.42	< 2.40	4.31	< 2.44	<2.43	<2.41	<2.48	
1-methylphenanthrene	8.87	7.22	<2.44	< 2.44	<2.38	< 2.47	< 2.43	<2.47	<2.42	< 2.40	<2.43	< 2.44	<2.43	<2.41	<2.48	
2-methylmaphthalene	1.51	1.50	<2.44	<2.44	<2.38	< 2.47	< 2.43	6.97	<2.42	< 2.40	<2.43	< 2.44	<2.43	<2.41	<2.48	
C1-fluoranthenes & pyrenes	46.6	29.5	<2.44	<2.44	<2.38	< 2.47	< 2.43	<2.47	<2.42	< 2.40	<2.43	< 2.44	<2.43	<2.41	3.05	
C1-phenan threnes & anthracenes	26.0	20.0	<2.44	<2.44	<2.38	< 2.47	13.40	<2.47	<2.42	< 2.40	<2.43	< 2.44	2.63	<2.41	<2.48	
C1-chrysenes	40.2	34.5	<2.44	<2.44	<2.38	< 2.47	< 2.43	<2.47	<2.42	< 2.40	<2.43	< 2.44	<2.43	<2.41	<2.48	
C1-dibenzot hiophenes	1.49	1.24	<2.44	<2.44	<2.38	<2.47	<2.43	<2.47	<2.42	< 2.40	<2.43	<2.44	<2.43	<2.41	<2.48	
C1-fluorenes	4.10	2.94	3.94	<2.44	<2.38	<2.47	10.10	2.55	<2.42	2.75	39.9	13.8	< 2.43	< 2.41	2.57	
C1-napht halenes	2.67	2.39	<2.44	<2.44	<2.38	<2.47	3.30	14.40	2.62	< 2.40	6.06	< 2.44	<2.43	<2.41	<2.48	
C2-phenan threnes & anthracenes	7.48	8.18	<2.44	<2.44	<2.38	<2.47	< 2.43	< 2.47	<2.42	< 2.40	<2.43	<2.44	< 2.43	< 2.41	<2.48	
C2-chrysenes	8.53	10.2	<2.44	<2.44	<2.38	<2.47	< 2.43	< 2.47	<2.42	< 2.40	<2.43	<2.44	< 2.43	<2.41	<2.48	
C2-fluorenes	3.23	1.80	3.70	<2.44	<2.38	<2.47	2.54	< 2.47	<2.42	< 2.40	2.61	<2.44	< 2.43	<2.41	<2.48	
C2-napht halenes	1.72	1.92	<2.44	<2.44	<2.38	<2.47	4.99	<2.47	2.81	<2.40	10.20	<2.44	<2.43	<2.41	<2.48	
C3-phenth renes & anthrac enes	2.83	3.49	<2.44	<2.44	<2.38	<2.47	< 2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	<2.48	
C3-chrysenes	1.29	2.08	<2.44	<2.44	<2.38	<2.47	< 2.43	< 2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	<2.48	
C3-fluorenes	<1.25	<1.24	12.30	<2.44	<2.38	<2.47	<2.43	< 2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	2.80	
C3-napht halenes	1.44	<1.24	<2.44	<2.44	<2.38	<2.47	4.16	<2.47	<2.42	<2.40	7.20	<2.44	<2.43	<2.41	<2.48	
C4-phenan threnes & anth racenes	<1.25	1.40	<2.44	<2.44	<2.38	<2.47	< 2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	<2.48	
C4-chrysenes	4.34	4.09	<2.44	<2.44	<2.38	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	<2.48	
Acenaphthalene	3.03	3.29	<2.44	<2.44	<2.38	<2.47	< 2.43	< 2.47	<2.42	<2.40	3.24	<2.44	<2.43	<2.41	<2.48	
Acenaphthene	14.0	7.58	20.90	<2.44	<2.38	<2.47	32.10	<2.47	<2.42	<2.40	80.10	<2.44	<2.43	<2.41	<2.48	
Anthracene	4.07	3.82	<2.44	<2.44	<2.38	<2.47	3.31	3.57	2.81	2.48	8.17	<2.44	<2.43	<2.41	3.41	
Benzo (a,) anth raacene	117.	92.20	<2.44	<2.44	<2.38	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	4.38	
Benzo (a) pyrene	222.	151.	<2.44	<2.44	4.34	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	3.17	<2.41	8.19	
Benzo (b) fluoranthene	173.	121.	2.48	<2.44	5.73	<2.47	<2.43	4.96	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	12.60	
Benzo (e) pyrene	102.	66.0	<2.44	<2.44	3.04	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	7.05	
Benzo (g,h,i) perylene	128.	84.0	2.49	<2.44	3.84	<2.47	<2.43	<2.47	<2.42	<2.40	< 2.43	<2.44	2.85	<2.41	9.07	

Appendix 9 (Cont.). Polyaromatic hydrocarbons in sediment and crayfish collected from two locations in Granite Creek, Arizona, 2000.

		Sample type, date and location collected and contaminant concentration, ppb wetweight													
	Sedi	ment <sup>2</sup>		Cray	rfish³			Green	sunfish <sup>4</sup>			Golden	shiner <sup>5</sup>		Tadpole <sup>6</sup>
	06/1	4/01	04/2	8/01	06/1	4/01	04/2	28/01	06/1	4/01	04/2	28/01	06/1	4/01	06/14/00
Compoound	Up- stream	Down- stream	Up- stream	Down- stream	Up- stream	Down- stream	Up- stream	Down- stream	Up- stream	Down- stream	Up- stream	Down- stream	Up- stream	Down- stream	Down- stream
Benzo (k) fluoranthene	48.3	36.8	<2.44	<2.44	<2.38	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	2.46	<2.41	5.20
Biphen yl	<2.44	<2.44	<2.44	<2.44	<2.38	<2.47	3.22	5.37	<2.42	<2.40	7.56	<2.44	<2.43	<2.41	<2.48
Chrysene	162.	103.	4.16	<2.44	4.86	<2.47	<2.43	5.18	<2.42	<2.40	<2.43	<2.44	2.70	<2.41	8.89
Dibenzo (a,h) anthracene	26.2	17.5	<2.44	<2.44	<2.38	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	<2.48
Dibenzothiophene	5.53	3.48	<2.44	<2.44	<2.38	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	<2.48
Fluoranthene	281.	182.	8.20	<2.44	7.81	4.23	3.62	14.70	<2.42	<2.40	3.26	<2.44	4.26	<2.41	13.70
Fluorene	18.30	10.60	11.70	<2.44	<2.38	<2.47	31.40	<2.47	<2.42	<2.40	75.0	<2.44	<2.43	<2.41	10.60
Indeno (1,2,3-c,d) pyrene	141.	90.3	2.47	<2.44	3.47	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	7.70
Naphthalene	4.33	4.53	<2.44	<2.44	<2.38	<2.47	<2.43	30.40	<2.42	2.60	3.62	<2.44	2.61	<2.41	<2.48
Perylene	27.0	21.5	<2.44	<2.44	<2.38	<2.47	<2.43	<2.47	<2.42	<2.40	<2.43	<2.44	<2.43	<2.41	<2.48
Phenanthrene	176.	114.	3.68	<2.44	5.97	2.48	2.73	8.81	2.98	3.89	2.79	<2.44	2.52	<2.41	8.08
Pyrene	260.	172.	6.82	<2.44	7.06	3.72	<2.43	4.20	<2.42	<2.40	<2.43	<2.44	4.06	<2.41	11.90
Pentachloropenol	21.2	5.44	<9.77	<9.78	<9.52	<9.86	<9.72	<9.87	<9.66	32.2	<9.72	<9.77	<9.71	<9.65	315
Pentachloro-anisole	0.18	< 0.12	0.50	< 0.24	< 0.24	< 0.25	3.93	1.60	0.60	0.86	6.52	3.76	0.32	0.27	1.18

<sup>1,6,7-</sup>trimethyl-naphthalene, 2,6-dimethylnaphthalene and C2-dibenzothiophenes were not detected in any samples.

<sup>&</sup>lt;sup>2</sup>One sediment sample was collected per site.

<sup>&</sup>lt;sup>3</sup>Crayfish collected 4/28/01: Site 1, N= 7, moisture = 78.0%, lipids = 1.60%; Site 2, N = 2, moisture = 76.4%, lipids = 0.50%

 $Cray fish\ collected\ 6/14/01:\ Site\ 1,\ N=8,\ moisture=79.4\%,\ lipids=2.40\%;\ Site\ 2,\ N=4,\ moisture=74.8\%,\ lipids=1.40\%.$ 

<sup>&</sup>lt;sup>4</sup>Green sunfish collected 4/28/01: Site 1, N = 18, moisture = 77.5%, lipids = 1.60%; Site 2, N = 11, moisture = 75.0%, lipids = 390.%. Green sunfish collected 6/14/01: Site 1, N = 10, moisture = 74.4%, lipids = 2.90%; Site 2, N = 15, moisture = 78.3%, lipids = 4.20%.

<sup>&</sup>lt;sup>5</sup>Golden shiner collected 4/28/01: Site 1, N = 13, moisture = 75.3%, lipids = 3.10%; Site 2, N = 12, moisture = 72.6%, lipids = 2.60%.

Golden shiner collected 6/14/01: Site 1, N = 10, moisture = 80.6%, lipids = 0.80%; Site 2, N = 10, moisture = 77.6%, lipids = 1.20%.

<sup>&</sup>lt;sup>6</sup>Bullfrog tadpole: N= 6, moisture = 85.6%, lipid = 2.60%.

Appendix 10. Dioxin-like compounds in sediment, invertebrates, and fish collected from Granite Creek and Watson Lake, Arizona, 2000-2001.

	Concentration, parts per billion, wet weight													
Sample	Area coll.	1,2,3,4, 6,7,8- HpCDD	1,2,3,4, 7,8- HxCDD	1,2,3,6, 7,8- HxCDD	1,2,3,7, 8,9- HxCDD	1,2,3,7,8- PeCDD	2,3,7,8- TCDD	OCDD	Moist (%)	Lipid (%)				
Sediment	Site 1	.756	.006	.027	.016	.002	.00050	.93	23.1	NA				
Sediment	Site 2	.580	.004	.019	.010	<.001	.00050	.98	29.5	NA				
Crayfish	Site 1	.029	<.005	.005	<.005	<.005	<.00094	.198	78.0	1.60				
Crayfish	Site 1	.057	<.005	.011	<.005	<.005	<.00095	.315	79.4	2.40				
Crayfish	Site 2	.018	<.005	<.005	<.005	<.005	<.00098	.154	76.4	0.50				
Crayfish	Site 2	.022	<.0055	<.005	<.005	<.005	<.00091	.141	74.8	1.40				
Tadpole	Site 2	.128	<.005	.010	<.005	<.005	<.00098	.999	85.6	2.60				
Green sunfish	Site 1	<.005	<.005	<.005	<.005	<.005	<.00095	.031	77.5	1.60				
Green sunfish	Site 1	.005	<.005	<.005	<.005	<.005	<.00095	.012	74.4	2.90				
Green sunfish	Site 2	<.003	<.003	<.003	<.003	<.003	<.00065	.013	75.0	3.90				
Green sunfish	Site 2	.008	<.004	<.004	<.004	<.004	<.00085	.035	78.3	4.20				
Golden shiner	Site 1	.007	<.005	<.005	<.005	<.005	<.00096	.037	73.5	3.10				
Golden shiner	Site 1	.024	<.004	<.004	<.004	<.004	<.00087	.172	80.6	0.80				
Golden shiner	Site 2	<.004	<.004	<.005	<.005	<.005	<.00090	.018	72.6	2.60				
Golden shiner	Site 2	.015	<.005	<.005	<.005	<.005	<.00097	.112	77.6	1.20				

Appendix 11. Furan-like compounds in sediment, invertebrates, and fish collected from Granite Creek, Arizona, 2000-2001.

Concentration, parts per billion, wet weight												
Sample number	Area collected	1,2,3,4, 6,7,8- HpCDF	1,2,3,4, 7,8,9- HpCDF	1,2,3,4, 7,8- HxCDF	1,2,3, 6,7,8- HxCDF	1,2,3, 7,8- PeCDF	2,3,4, 6,7,8- HxCDF	2,3,7,8- TCDF	OCDF	Moist (%)	Lipid (%)	
Sediment	Site 1	.167	.010	.007	.003	<.001	.006	<.00022	.534	23.1	NA	
Sediment	Site 2	.120	.006	<.001	.002	<.001	.004	<.00024	.394	29.5	NA	
Crayfish	Site 1	0.10	<.005	<.005	<.005	<.005	<.005	<.00094	.019	78.0	1.60	
Crayfish	Site 1	.045	<.005	<.005	<.005	<.005	<.005	<.00095	.026	79.4	2.40	
Crayfish	Site 2	<.005	<.005	<.005	<.005	<.005	<.005	<.00098	.012	76.4	0.50	
Crayfish	Site 2	.019	<.005	<.005	<.005	<.005	<.005	<.00091	.012	74.8	1.40	
Tadpole	Site 2	.071	<.005	<.005	<.005	.008	<.005	<.00098	.081	85.6	2.60	
Green sunfish	Site 1	.066	<.005	<.005	<.005	.009	<.005	<.00095	<.009	77.5	1.60	
Green sunfish	Site 1	.027	<.005	<.005	<.005	<.005	<.005	<.00095	<.010	74.4	2.90	
Green sunfish	Site 2	.017	<.003	<.003	<.003	<.003	<.003	<.00065	<.007	75.0	3.90	
Green sunfish	Site 2	.100	<.004	<.004	<.004	.013	<.004	<.00085	<.008	78.3	4.20	
Golden shiner	Site 1	.027	<.005	<.005	<.005	<.005	<.005	.00110	<.010	73.5	3.10	
Golden shiner	Site 1	.026	<.004	<.004	<.004	<.004	<.004	<.00087	.016	80.6	0.80	
Golden shiner	Site 2	.026	<.005	<.005	<.005	.005	<.005	<.00090	<.009	72.6	2.60	
Golden shiner	Site 2	.055	<.005	<.005	<.005	.010	<.005	<.00097	.010	77.6	1.20	

<sup>&</sup>lt;sup>1</sup>1,2,3,7,8,9-HxCDF and 2,3,4,7,8-PeCDF were not detected in any samples.

REFERENCE TABLE 1. Pentachlorophenol (PCP) concentrations (ppb wet weight) in whole body crayfish and fathead minnows collected from Granite Cræk (Watson Woods) near Prescott, Arizona June 12, 1995.

Sample <sup>1</sup>	Area <sup>2</sup>	Percent lipid	PCP (ppb)
crayfish crayfish	1 2	2.06 1.84	<5.0 7.8
fathead minnow	1	6.66	10.0
fathead minnow	2	6.16	62.0

<sup>&</sup>lt;sup>1</sup>All samples are whole body composite.

 $<sup>^{2}</sup>$ Area 1 = midpoint in the Watson Woods study site opposite the existing wastewater treatment plant. Area 2 = the upstream site adjacent to, and immediately below the industrial park.

REFERENCE TABLE 2. Trace element and heavy metal concentrations in whole body fish and crayfish from Granite Creek, Prescott, Arizona, June 12, 1995.

Sample	Area <sup>3</sup>	Wet Dry <sup>4</sup>	Sample Wt (g)	N	Al	As	В	Ba	Conta			tion, ppm d Mg M	ry weight: In N		-	Sr	V	Zn	
NCBP 85 <sup>5</sup>	NA	Wet	NA	NA	NA	0.27	NA	NA	NA	1.0	NA	NA	NA	NA	NA	NA	NA	NA	34.2
Crayfish <sup>2</sup>	2 2	Dry Wet	206	9	413.5 125.0	0.51 0.15	ND	203 61	0.57 0.18	107. 32.3	432 131	2400. 726.	199. 60.	0.79 0.24	ND	ND	403. 122.	0.37 0.11	64.4 19.5
Crayfish	1 1	Dry Wet	115	6	133.9 34.7	<0.35 <0.09	ND	156 40	<0.39 <0.10	94.0 24.4	138 36.	1871. 485.	154. 40.	0.39 0.10	ND	ND	456. 118.	<0.39 <0.10	57.7 15.0
Fathead Minnow	2 2	Dry Wet	61	26	515.4 111.1	0.71 0.15	4.31 0.93	36. 8.	29.70 6.42	9.54 2.06	830 179	1731. 373.	86 19	8.77 1.89	0.69 0.15	1.13. 0.25	57 12	1.00 0.22	145.0 31.2

Beryllium, cadmium, mercury, molybdenum, tin was not detected in any samples. Boron (4.31  $\mu$ g/g dry weight and 0.93  $\mu$ g/g wet weight), lead (0.69  $\mu$ g/g dry weight and 0.15  $\mu$ g/g wet weight), and selenium (1.13  $\mu$ g/g dry weight and 0.25  $\mu$ g/g wet weight) were detected only in the fathead minnow sample.

<sup>&</sup>lt;sup>2</sup>All samples are whole body composite.

<sup>&</sup>lt;sup>3</sup>Area 1 = midpoint in the Watson Woods study site opposite the WWTP. Area 2 = the upstream site adjacent to, and immediately below the industrial park.

<sup>&</sup>lt;sup>4</sup>Wet weight or dry weight basis.

<sup>&</sup>lt;sup>5</sup>NCBP 85th percentile (Schmitt and Brumbaugh 1990).